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J. STENHOUSE, LL.D., F.R.S.

Editor:

HENRY WATTS, B.A., F.C.S.

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CONTENTS OF THE EIGHTEENTH VOLUME.

PAGE

The Action of Ammonia on Sulphochloride of Phosphorus. By J. H. Gladstone, Ph.D., F.R.S., and J. D. Holmes, Esq. 1

Note on the Artificial Formation of Pyridine from Naphthalene. By W. H. Perkin..... 9

Researches on the Vacuum. By Hermann Sprengel, Ph.D. 9

On a New Reaction for the Production of Anhydrides and Ethers. By John Broughton, B. Sc., Chemical Assistant, Royal Institution 21

Laboratory Memoranda. By Robert Warington, Junr., Assistant to Professor of Chemistry, R. A. College, Cirencester 27

Note on the Boiling Points of Isomeric Ethers of the Formula $C_nH_{2n}O_2$. By J. Alfred Wanklyn..... 30

Note on the Action of Chloropicrin and Chloroform on Acetate of Potash. By Henry Bassett 31

On Microscopical Researches in Relation to Pharmacy. By Henry Deane, F.L.S , and Henry B. Brady, F.L.S..... 34

On the Oxidation of India Rubber. By John Spiller, F.C.S. 44

On a Dense Brine from Saltsprings, Nova Scotia. By Prof. How, D.C.L., University of King's College, Windsor, N.S. 46

On the most Volatile Constituents of American Petroleum. By Edmund Ronalds, Ph.D. 54

On the Action of Chlorine upon Arsenious Acid. By Charles L. Bloxam.. 62

On a Crystallised Hydrate of Phenylic Alcohol. By F. Crace Calvert, F.R.S., F.C.S. 66

On the Action of Silicate and Carbonate of Soda on Cotton Fibre. By F. Crace Calvert, F.R.S., F.C.S. 70

On some Hydrated Cupric Oxychlorides from Cornwall. By A. H. Church, M.A., Professor of Chemistry, R. A. College, Cirencester 77

On some Hydrated Cupric Oxysulphates from Cornwall. By A. H. Church . 83

On Vapour-Densities. By J. Alfred Wanklyn 89

Note on a New Bromine-Derivative of Camphor. By W. H. Perkin..... 92

On the Action of Hydrosulphate of Ammonia upon freshly precipitated Sulphide of Copper. By Charles L. Bloxam 94

Notes upon the General Routine of Qualitative Analysis for Metals. By Charles L. Bloxam..... 97

On the Periodides of some of the Organic Bases. By William A. Tilden, Demonstrator of Chemistry in the Laboratory of the Pharmaceutical Society 99

On Phosphide of Magnesium. By Thomas P. Blunt 106

On the Specific Refractive Energy of Elements and their Compounds. By J. H. Gladstone, Ph.D., F.R.S. 108

PAGE

Observations on some Points in the Analysis of Potable Waters. By Professor W. A. Miller, M.D., LL.D., Pres. Chem. Soc.; Treas. and V.P.R.S. 117

Researches on Acids of the Acrylic Series.—No. 1. Transformation of the Lactic into the Acrylic Series of Acids. By E. Frankland, F.R.S., and B. F. Duppa, Esq. 133

On Lecture Illustrations. By A. W. Hofmann 156

On the Action of Nascent Hydrogen on Azodinaphthyldiamine. By W. H. Perkin 173

On a Mode of Measuring the Relative Sensitiveness of Photographic Papers. By Arthur M'Dougall, B.Sc. 183

On some Compounds and Derivatives of Glyoxylic Acid. By Henry Debus, Ph.D., F.R.S. 193

On the presence of Manganese in Oolite and Lias. By Robert Warington, Junr., Assistant to Professor of Chemistry, Royal Agricutural College, Cirencester 206

Table for the Calculation of direct Nitrogen Determinations. By Jas. T. Brown 210

Notes on a Cornish Mineral of the Atacamite Group. By A. H. Church 212

Notes on a Ferric Hydrate from Cornwall. By A. H. Church 214

Analyses of some Bronzes found in Great Britain. By A. H. Church 215

The Estimation of Indigotin, or the Blue Colouring Matter of Indigo. By Clemens Ullgren 217

On the Qualitative Analysis of Substances Insoluble in Water and Acids. By Charles L. Bloxam 226

On the Theory of Isomeric Compounds. By Dr A. Crum Brown 230

On the Action of Light upon Sulphide of Lead, and its bearing upon the Preservation of Paintings in Picture Galleries. By Dr. David S. Price, F.C.S. 245

Notes on the Compounds of Copper and Phosphorus. By F. A. Abel, F.R.S. 249

Chemical Researches on some new and rare Cornish Minerals. By A. H. Church, M.A., Professor of Chemistry Royal Agricultural College, Cirencester 259

On a new Series of Bodies in which Nitrogen is substituted for Hydrogen. By Peter Griess 268

On the Decay of Gutta-percha and Caoutchouc. By Professor William Allen Miller, F.R.S. 273

On the Absorption of Vapours by Charcoal. By John Hunter, M.A. 285

On Caprylic and Œnanthylic Alcohols. By Ernest T. Chapman 290

On a New Class of Organic Compounds in which Hydrogen is replaced by Nitrogen. By Peter Griess 298

On Nitro-compounds (Part II). With Remarks on Isomerism. By Edmund J. Mills, D.Sc., F.C.S. 319

On the Synthesis of Tribasic Acids. By Maxwell Simpson, M.D., F.R.S. 331

On an Ammoniacal Deposit formed in the process of Drying Blood. By John A. R. Newlands, F.C.S. 340

JOURNAL

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THE CHEMICAL SOCIETY.

I.—*The Action of Ammonia on Sulphochloride of Phosphorus.*

By J. H. Gladstone, Ph.D., F.R.S., and J. D. Holmes, Esq.

During the continuation of the researches referred to in a previous paper * we have examined the action of ammonia on sulphochloride of phosphorus. Schiff † had previously stated that there results a white mass which is decomposed very quickly by cold water, and evolves sulphuretted hydrogen when treated with hot water. He supposed it to contain, in addition to chloride of ammonium, sulphosphotriamide, $\left.\begin{matrix} PS''' \\ H_3 \\ H_3 \end{matrix}\right\} N_3$, but he gives no analyses. He states also that, when heated without access of air, this white mass gives off ammonia, while there remains a white substance difficult to decompose.

We found that when dry ammoniacal gas was passed into a flask containing pure sulphochloride of phosphorus, at the ordinary temperature, four equivalents were the most that it would absorb. At 0°C. the same amount was absorbed, though more slowly, and when heated to almost the point of decomposition, it absorbed no more. The following were the results of experiment:—

* Chem. Soc. J. [2], ii, 225.

† Ann. Ch. Pharm., ci., 303.

3·713 grms.	PCl_3S	absorbed	1·485 grm.	NH_3	= 39·9 p.c.
5·327	„	„	2·180	„	= 40·9 „
4·142	„	„	1·685	„	= 40·7 „
3·160	„	„	1·282	„	= 40·6 „

Now 4 equivalents of ammonia would cause an increase in weight of 40·3 per cent.

The result is a white substance, caked together, dissolving entirely in water, except perhaps a trace of the sulphochloride, and yielding then an acid solution. The solution gives no indication of phosphoric acid when tested with ammonia and sulphate of magnesium, nor does it contain any trace of sulphuretted hydrogen. When rendered neutral, it gives precipitates with several metallic salts.

With sulphate of copper it gives a yellowish-white flocculent precipitate, insoluble in dilute hydrochloric acid or ammonia, soluble in cyanide of potassium; it becomes brown on drying: when heated *per se* in a tube, it gives off ammonia and sulphide of ammonium.

With sulphate of zinc, it gives also a white flocculent precipitate readily soluble in dilute acids and ammonia; it suffers the same decomposition when heated *per se*.

With chloride of cadmium it gives a similar precipitate.

With chloride of lead, a white precipitate was obtained, soluble in dilute nitric acid. The precipitate when boiled with water slowly turned black.

With sulphate of nickel, a greenish-white precipitate was produced, readily soluble in dilute acids and ammonia. The ammoniacal solution when boiled deposited sulphide of nickel.

With chloride of cobalt, it gave an exactly similar precipitate of a bluish-white colour.

A solution of protochloride of tin produced a bulky white precipitate, readily soluble in dilute hydrochloric acid.

Nitrate of silver gives a white precipitate mixed with chloride of silver. This precipitate is insoluble in dilute nitric acid and in ammonia; the presence of an excess of nitrate of silver causes it to turn black.

No precipitates were obtained with solutions of chloride of barium, chloride of calcium, sulphate of magnesium, ferric chloride or sulphate of aluminum.

With chloride of mercury it gave a bulky white precipitate, but

this soon changed to a yellow one, which was found to be nothing else than the compound of sulphide and chloride of mercury, $Hg_2S.HgCl$. It forms no black sulphide of mercury, even if the sulphur acid in solution be in large excess. The solution from this yellow precipitate gives no precipitate with ammonia and sulphate of magnesium, and probably contains an amidated acid; but we have not yet submitted it to a complete examination.

The copper, cadmium, and zinc salts were well washed, dried, and analysed. The process adopted was as follows:—To determine the metal, sulphur, and phosphorus, the salt was oxidized with fuming nitric acid till completely dissolved, and the sulphuric acid formed was precipitated by chloride of barium; after separating the excess of barium, the metal was precipitated by sulphuretted hydrogen or sulphide of ammonium, and the phosphoric acid in the filtrate was determined in the usual manner as magnesium-salt. To determine the nitrogen, the salt was digested with hydrochloric acid for some time till completely decomposed, the copper or cadmium precipitated by sulphuretted hydrogen, and the nitrogen determined as ammonio-platinum-salt in the filtrate. The cadmium was weighed as sulphide, but the sulphides of copper and zinc were re-dissolved, and weighed as oxides.

Copper-salt.

I. ·4205 grm. gave ·675 grm. $Ba_2S\Theta_4$, ·1195 grm. $Cu_2\Theta$, and 322 grm. $Mg_4P_2\Theta_7$.

II. ·2455 grm. gave ·0695 grm. $Cu_2\Theta$ and ·7515 grm. $PtCl_2,NH_4Cl$.

III. ·297 grm. gave ·0835 grm. $Cu_2\Theta$ and ·915 grm. $PtCl_2.NH_4Cl$.

IV. ·549 grm. ignited with oxide of copper gave ·1475 grm. $H_2\Theta$.

These numbers reckoned to 100 parts give:—

	I.	II.	III.	IV.
Phosphorus	21·38	—	—	—
Nitrogen	—	19·19	19·31	—
Hydrogen	—	—	—	2·98
Copper.....	22·67	22·59	22·49	—
Sulphur	22·02	—	—	—

This agrees with the composition $PN_2H_4Cu S\Theta$, which we may term the thiophosphodiamate of copper.

		Calculated.	Mean of analyses.
Phosphorus	31	21·74	21·38
Nitrogen	28	19·64	19·25
Hydrogen.....	4	2·80	2·98
Copper.....	31·6	22·16	22·58
Sulphur	32	22·44	22·02
Oxygen.....	16	11·22	11·79 (by loss)
	142·6	100·00	100·00

Cadmium-salt.

I. ·2795 grm. gave ·1195 grm. Cd_2S, and ·7655 grm. $PtCl_2.NH_4Cl$.

II. ·338 grm. gave ·144 grm. Cd_2S, ·488 grm. Ba_2SO_4, and ·2295 grm. $Mg_4P_2O_7$.

III. ·265 grm. gave 114 grm. Cd_2S, and ·725 grm. $PtCl_2.NH_4Cl$.

IV. ·405 grm. ignited with oxide of copper gave ·0855 grm. H_2O.

Or in 100 parts:—

	I.	II.	III.	IV.
Phosphorus....	—	18·96	—	—
Nitrogen.....	17·18	—	17·15	—
Hydrogen	—	—	—	2·34
Cadmium	33·25	33·13	33·46	—
Sulphur	—	19·78	—	—

This agrees equally with the formula PN_2H_4CdSO, thio-phosphodiamate of cadmium.

		Calculated.	Mean of analyses.
Phosphorus	31	18·57	18·96
Nitrogen.....	28	16·76	17·16
Hydrogen	4	2·40	2·34
Cadmium	56	33·53	33·28
Sulphur	32	19·16	19·78
Oxygen	16	9·58 (by loss)	8·48
	167	100·00	100·00

Zinc-salt.

I. ·607 grm. gave ·9705 grm. Ba_2SO_4, ·169 grm. Zn_2O, and ·4745 grm. $Mg_4P_2O_7$.

II. ·1775 grm. gave ·546 grm. $PtCl_2.NH_4Cl$.

These determinations agree with the formula PN_2H_4ZnSO.

	Calculated.		I.	II.
Phosphorus	31	21·60	21·82	—
Nitrogen	28	19·52	—	19·29
Hydrogen.....	4	2·78	—	—
Zinc	32·5	22·65	22·28	—
Sulphur.....	32	22·30	21·94	—
Oxygen.....	16	11·15	—	—
	143·5	100·00		

Two attempts were made to obtain the acid itself in a fit state for analysis. The mixed thio-phosphodiamate and chloride of silver was treated with hydrochloric acid, and the thio-phosphodiamate of copper was treated with sulphuretted hydrogen, and in each case the filtered solution was allowed to evaporate over sulphuric acid. The solutions, which were very feebly acid to test-paper, continued to deposit sulphur for some days, when they appeared to contain the ammonium-salt of some amidated phosphoric acid. That the acid can exist for awhile in a free state is evident from the mode of preparation.

A portion of sulphochloride of phosphorus, instead of being treated with gaseous ammonia, was thrown into the strongest aqueous solution of that gas. A clear solution resulted, which, when neutralised, gave a copper-salt similar to that previously examined, but on analysis it yielded 27·7 per cent. of copper and 12·2 per cent. of nitrogen. Thinking it might be a mixture of thio-phosphodiamate of copper with a salt containing a smaller amount of amidogen, we varied the mode of preparation. The very strong aqueous ammonia was mixed with about an equal bulk of water, and the sulphochloride was thrown into it and shaken well with it. It slowly disappeared, and the neutralised solution gave the following reactions:—

With sulphate of copper, a yellowish-white precipitate insoluble in dilute hydrochloric acid or ammonia; it becomes dark-brown while drying.

With solution of chloride of lead a white precipitate is produced, soluble in dilute nitric acid; it becomes pale-yellow when dry.

Chloride of cadmium produces a bulky white precipitate, soluble in excess of either precipitant, in dilute acids, and ammonia; when dry it was pale-yellow.

Sulphate of zinc produced a white precipitate which resembled the cadmium-salt in every particular.

A solution of protochloride of tin and potassium, produced a bulky white precipitate, soluble in hydrochloric acid.

No precipitates were obtained with solutions of nickel, cobalt, iron, aluminum, barium, calcium, or magnesium.

With chloride of mercury, it gave the yellow mercuric sulphochloride, and if the sulphur-acid was in excess, the black sulphide. This affords a reaction capable of distinguishing the present from the preceding acid.

The cadmium and lead salts were submitted to analysis :—

Cadmium-salt.

I.—·479 grm. gave ·309 Cd_2S, and ·477 grm. $PtCl_2NH_4Cl$.

II.—·4055 grm. gave ·2605 Cd_2S, ·435 grm. Ba_2SO_4, and ·201 grm. $Mg_4P_2O_7$.

III.—·957 grm. ignited with oxide of copper, gave ·0845 grm. H_2O.

These numbers reckoned to 100 parts give :—

	I.	II.	III.
Phosphorus.....	—	13·84	—
Nitrogen.....	6·24	—	—
Hydrogen	—	—	·98
Cadmium	50·17	49·96	—
Sulphur	—	14·50	—

This agrees almost exactly with what would be required by the formula $PNH_2Cd_2SO_2$, or thio-phosphamate of cadmium.

	Calculated.		Mean of analyses.
Phosphorus	31	13·90	13·84
Nitrogen	14	6·28	6·24
Hydrogen.....	2	·90	·98
Cadmium.....	112	50·22	50·07
Sulphur	32	14·35	14·50
Oxygen.....	32	14·35	14·37 (by loss)
	223	100·00	100·00

Lead-salt.

I.—·412 grm. gave ·392 grm. Pb_2SO_4, and ·2825 grm. $PtCl_2NH_4Cl$.

II.—·248 grm. decomposed by fuming nitric acid, gave a white powder of sulphate of lead, which was collected after the

excess of nitric acid had been in a great measure driven off, and was washed with alcohol. It weighed ·236 grm. The solution yielded only the faintest traces of either lead or sulphuric acid.

III.—·2845 grm. gave ·271 grm. $Pb_2S\Theta_4$ and ·097 grm. $Mg_4P_2\Theta_7$.

IV.—·8765 grm. ignited with oxide of copper, gave ·054 grm. $H_2\Theta$.

Or in 100 parts :—

	I.	II.	III.	IV.
Phosphorus	—	—	9·52	—
Nitrogen	4·30	—	—	—
Hydrogen.....	—	—	—	·68
Lead.....	65·00	65·01	65·02	—
Sulphur	—	10·05	—	—

This also coincides with what should be given by thio-phosphamate of lead, $PNH_2Pb_2S\Theta_2$.

		Calculated.	Mean of analyses.
Phosphorus	31	9·75	9·52
Nitrogen	14	4·40	4·30
Hydrogen.....	2	·62	·68
Lead.....	207	65·09	65·01
Sulphur	32	10·07	10·05
Oxygen.....	32	10·07	10·44 (by loss)
	318	100·00	100·00

The two acids described above may be viewed as amidated sulphoxiphosphoric acids. Wurtz has shown that when sulphochloride of phosphorus is treated with an aqueous solution of potash or soda, there is produced a salt of a tribasic acid analogous to phosphoric acid, but containing one atom of oxygen replaced by sulphur. This acid seems even to be produced, though not so well by water alone. Now, when ammonia acts on the sulphochloride at the same time as water does, the acid produced contains NH_2 in place of $H\Theta$, and is bibasic. It might be called sulphoxiphosphamic acid; but in order somewhat to curtail the name we have preferred to call it thio-phosphamic acid. If, however, the aqueous ammonia is very strong indeed, or if the ammonia act on the sulphochloride of phosphorus first and water act afterwards, the acid produced contains two atoms of NH_2 in place of two of $H\Theta$,

and is monobasic. It is sulphoxiphosphodiamic or thio-phosphodiamic acid. The scheme of decomposition in the three cases is as follows :—

$$PCl_3S + 3H_2O = 3HCl + PH_3SO_3$$ thio-phosphoric acid

$$PCl_3S + NH_3 + 2H_2O = 3HCl + P(NH_2)H_2SO_2$$ thio-phosphamic acid

$$PCl_3S + 2NH_3 + H_2O = 3HCl + P(NH_2)_2HSO$$ thio-phosphodiamic acid.

But in practice of course, a large amount of ammonia is required, as ammoniacal salts and not free acids are produced; and in the production of thio-phosphodiamic acid there is an intermediate stage.

When sulphochloride of phosphorus is brought in contact with aqueous ammonia, 6 equivalents of ammonia take part in the reaction, thus :—

$$PCl_3S + 6NH_3 + 2H_2O = 3NH_4Cl + PNH_2(NH_4)_2SO_2;$$

or, if the ammonia be more concentrated, it seems probable we may have the reaction more or less according to the scheme :—

$$PCl_3S + 6NH_3 + H_2O = 3NH_4Cl + P(NH_2)_2NH_4SO.$$

When sulpho-chloride of phosphorus is brought in contact with dry ammonia, it is difficult to suppose that the four atoms of the gas act in any other way than by removing two atoms of chlorine and leaving two atoms of amidogen in their place, according to the equation:—

$$PCl_3S + 4NH_3 = 2NH_4Cl + P(NH_2)_2ClS.$$

This latter compound we have not succeeded in separating from the chloride of ammonium that accompanies it; but supposing it to exist as a distinct substance, the formation of thio-phosphodiamic acid from it by means of water is of the simplest character, namely, the replacement of the chlorine by HO, thus :—

$$P(NH_2)_2ClS + H_2O = HCl + P(NH_2)_2HSO.$$

II.—*Note on the Artificial Formation of Pyridine from Naphthalene.*

By W. H. Perkin.

As mentioned some time since,* azodinaphthyldiamine, when treated with nascent hydrogen, is decolorized, and yields one or more bases possessing peculiar characters. Amongst these I have found pyridine, and have obtained sufficient for the preparation of its platinum-salt, a platinum-determination of which gave 35·02 per cent., theory requiring 34·60. The platinum-salt thus obtained gave when boiled the sulphur-yellow so-called bihydrochlorate, and also when heated, fused, and intumesced in the same manner as the platinum-salt of the pyridine obtained from Dippel's oil. The base has also its characteristic odour, and is not in the least decomposed by fuming nitric acid.

I hope shortly to bring before the Society a more particular account of this and the other bases which accompany it, in the reaction above alluded to.

III.—*Researches on the Vacuum.*

By Hermann Sprengel, Ph.D.

1. *The Instruments.*

The methods hitherto proposed for producing a vacuum may be divided into two classes, the mechanical and the chemical. A gas which fills a space may either be removed mechanically, or it may be converted, by taking advantage of its chemical or physical properties, into a non-gaseous, tensionless body. As however our atmosphere, from its general presence, is for the most part the only gas which has to be considered when a vacuum is to be formed, and as the reduction of its constituents to the non-gaseous form is attended with peculiar difficulties, I am inclined to consider that all practical methods of producing a vacuum may be regarded as mechanical. Atmospheric air may in fact be expelled from a space, firstly, by a solid

* Chem. Soc. J., vol. ix, p. 1.

body, secondly, by a liquid, and thirdly by a gas, which afterwards takes either a liquid or a solid form. Perfect vacua have hitherto been obtained only by this last method, but with such attending difficulties, that it appeared to me highly desirable to improve the other two, which afford greater facilities of working. The displacement of a gas by means of a solid or a liquid body is effected by instruments, commonly called air-pumps. The exhausting syringe of Otto von Guerïcke, with its piston, is the type of one class of these instruments, while Toricelli's barometer, with its column of mercury, is the type of the other class. The invention of the common air-pump was a consequence of Toricelli's vacuum, and it is partly due to this, that the degree of exhaustion attained by it has been, up to the present day, compared with Toricelli's vacuum as the standard of perfection. Hence it has followed that physicists have from time to time attempted to use Toricelli's vacuum as a receiver, or in other words to fill receivers with mercury, and attach tubes to them as long as those of barometers, through which the mercury was allowed to run off. All so-called mercurial air-pumps are based upon this principle, and differ very little from the famous experiment which Toricelli made 220 years ago.

This, however, is not the only way in which the case may be viewed. If the top of a barometer were knocked off, the air would enter and the mercury would sink, or what is the same, the mercury would sink and draw in the air. If, however, the experiment be so arranged as to allow air to enter, together with the mercury, and in such a manner that the supply of air shall be limited, while that of mercury is unlimited, the air will be carried away, and a vacuum produced. It is upon this principle that I have constructed a pneumatic machine, of which Fig. 1. represents the simplest form.

cd is a glass tube, longer than a barometer, open at both ends, and in which mercury is allowed to fall down, supplied by the funnel *A*, with which the tube is connected at *c*. The lower end, *d*, of this tube dips into a small glass bulb, *B*, into which it is fixed by means of a cork. This glass bulb has a spout at its side, situated a few millimetres higher than the lower end of the tube *c d*. The first portions of mercury which run down, will consequently close the tube, and form a safeguard against the air, which might enter from below, if the equilibrium should be disturbed. The upper part of *cd* branches off at *x* into a lateral

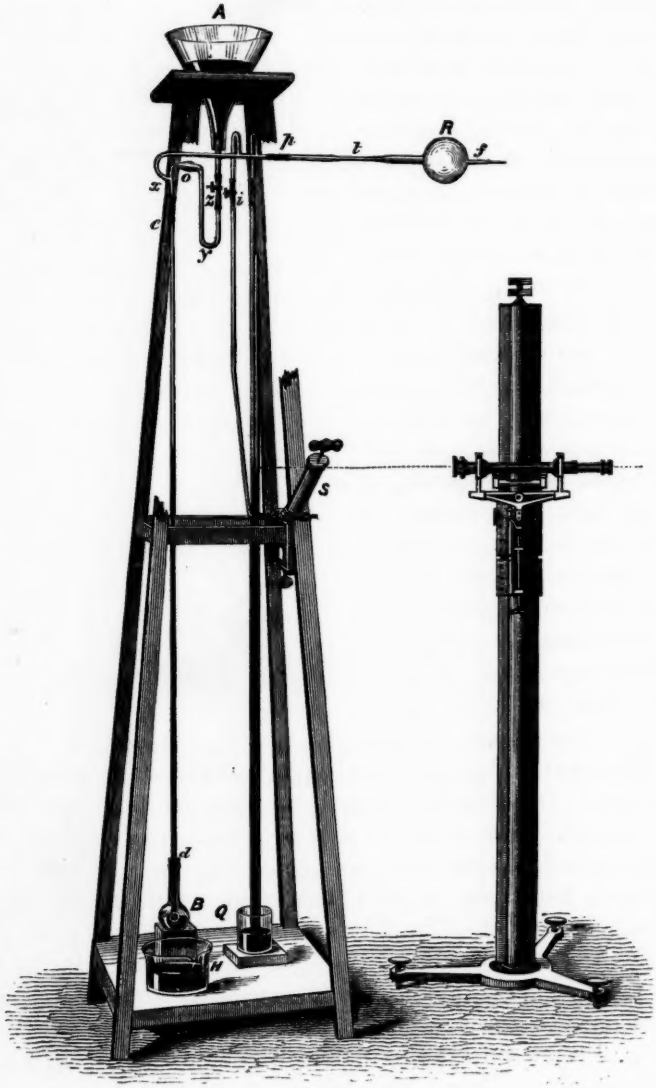
tube, to which the receiver *R* is affixed. As soon as the stop-cock at *c* is opened, and the mercury allowed to run down, the exhaustion begins, and the whole length of the tube, from *x* to *d*, is seen to be filled with cylinders of mercury and air, having a downward motion. Air and mercury escape through the spout of the bulb *B*, which is above the basin, *H*, where the mercury is collected. This has to be poured back from time to time into the funnel *A*, to pass through the tube again and again, until the exhaustion is completed. As the exhaustion is progressing, it will be noticed that the enclosed air between the mercury cylinders becomes less and less, until the lower part of *c d* presents the aspect of a continuous column of mercury, about 30 inches high. Towards this stage of the operation, a considerable noise begins to be heard, similar to that of a shaken water-hammer, and common to all liquids shaken in a vacuum. The operation may be considered completed, when the column of mercury does not enclose any air, and when a drop of mercury falls upon the top of this column without enclosing the slightest air-bubble. The height of this column now corresponds exactly with the height of the column of mercury in the barometer; or, what is the same, it represents a barometer, whose Toricellian vacuum is the receiver *R*.

FIG. 1.

Fig. 2 represents the actual instrument, with which I am in the habit of working. The funnel *A*, supported by a wooden stand, serves as the reservoir for the mercury. By means of the tube *z y x*, it is connected with the tube *c d*, which I call the

"fall tube," so that the mercury will run down, as soon as the clamp *z* is opened, which compresses a caoutchouc tube inserted

Fig. 2.



there. The tube *x p* leads to the receiver, which is to be exhausted, and is in connection with two tubes, one of which is attached to

the common exhausting syringe *S*, while the other, serving as a guage, dips into a glass of mercury, containing a barometer. When the instrument is at work, the rising of the mercury in this guage will consequently show the degree of exhaustion. The exhausting syringe is merely attached as an auxiliary, to accelerate the operation, because the fall-tube, for a reason to be presently mentioned, must be of a thin calibre. The greater portion of air is more quickly removed by the syringe, and after this has been done, as much as possible, and the connection between the receiver and the syringe has been broken off by compressing an inserted caoutchouc tube with the clamp *i*, the remainder of the air is carried off by the running mercury. The bulb *B*, and the basin *H* are exactly as in Fig. 1. The instrument is about 6 feet high, so that the mercury collected in the basin *H* can easily be poured back into the funnel *A*. The use of a pump would facilitate the raising of the mercury, and prevent the admixture of air. This latter inconvenience may, however, be pretty well overcome by gently pouring the mercury on a glass plate, floating on the surface of that in the funnel. Should a few air-bubbles attach themselves to the side of the funnel, it may be best to remove them by means of a wire or a glass-rod, though they are not, perhaps, of much consequence, as they are not observed to pass along with the mercury. The connections between the glass tubes are made of well-fitting black vulcanised caoutchouc tubing, sold under the name of "French tubing." This is free from metallic oxides, which render the tubing porous. Besides this, all these joints are bound with coils of copper wire, which is easily accomplished with a pair of pliers. Moreover, the space between the inside of the caoutchouc tubing and the outside of the glass tubing, is filled with a resinous cement made of fused caoutchouc. To prevent this substance soiling the interior of the instrument, I first, after having put the instrument together, tie the caoutchouc joint with the copper wire, and then turn back the end of the caoutchouc tubing over the coil, coat the inside of the end with the cement, and turn it back again into its proper position. From this it is obvious that the fused caoutchouc can only penetrate as far as the copper wire coil. The connection of the funnel with the tube *z y o* is made by means of a perforated caoutchouc cork. (These corks are easily made from a flat block of caoutchouc, cut out with a sharp Mohr's cork-borer, well lubricated with oil). When the instrument has been put together in this manner, it is ready for

use. At first the mercury is allowed to enter the fall-tube in such quantities as to raise the mercury in the guage as quickly as possible. When, however, the operation approaches its completion, which is shown by the rattling noise, it will be found useful to lessen the supply of mercury, and to let it fall down drop by drop on the column of mercury in the lower part of the fall-tube, and to proceed in this way till the exhaustion is completed. I am not able to give any definite statement as to the quantity of mercury to be employed, as it is obvious that a small quantity, say an ounce or two, is capable of exhausting a receiver of an indefinite size, if this mercury is only made to pass the fall-tube often enough; but I may remark that I have found 10 to 15 lbs. of mercury a convenient quantity to work with.

In my endeavours to find out how to construct the instrument, in order to exhaust a receiver, with the greatest economy of time and mercury, I have not met with satisfactory results. There, of course, exists a certain relation between the amount of air to be exhausted, the quantity of mercury to be employed, and the time of the operation. In order to make the instrument act at all, the supply of mercury must be at least so large that the fall-tube may become closed, *i. e.*, the running mercury may form drops of a cylindrical shape, breaking off the communication between the receiver and the external air. As the supply of mercury is increased, the rapidity with which the air is carried off also increases. But this soon reaches its limit, as, should the mercury be admitted too rapidly into the fall-tube, it gains the preponderance, and closes the aperture at *x*. The most favourable conditions under which the instrument might be used are those where the mercury is made to fall down drop by drop, enclosing between every two drops as large a portion of air as possible.

Volume may be increased by extension either in height or in breadth. If the fall-tube be lengthened, the bulk of the enclosed air will be increased, and the time required to produce exhaustion will be shortened, without increasing the weight of mercury employed. But as it is inconvenient to have the instrument higher than the height of a man, I attempted to increase the second dimension, viz., the width of the tubes. I soon found, however, that it was difficult, if not impossible, to close tubes of more than a certain width by single drops. In order to close a wide tube with a cylinder of mercury (or any other liquid), the mercury (or this other liquid) must run in freely and not in drops, for the simple

reason that drops cannot be formed of the diameter of the calibre of the tube. The size of the drops depends, upon the specific attraction of the molecules of the liquid, the form and surface of the vessel from which the liquid drops, the attraction existing between the liquid and the vessel, and the resistance offered by the greater or less density of the air through which the drop falls. I have not been able to form in a vacuum drops of mercury larger than about 3 millimetres in diameter.

Having failed in the use of a wide fall-tube, I endeavoured to effect my object by the use of several small fall-tubes. Here, however, another obstacle offered itself. It is exceedingly difficult to regulate the flow of mercury so evenly that exactly the same quantity shall run down in each separate fall-tube, and I have found in practice, that unless the flow of mercury can be so regulated, simultaneous action cannot be obtained in the fall-tubes.

From these experiments, I have found myself unable to produce a vacuum as quickly as with a common exhausting syringe, unless by the employment of inconveniently large quantities of mercury at a time. If speed is required, I think the fall-tube should have the addition of the exhausting syringe, which will take away more quickly the larger quantity of air and leave to the running mercury only the task of completing the exhaustion. By such a combination, however, the instrument loses much of its simplicity, and offers by its numerous joints a far greater chance of leakage. For this reason, where time is no object, it will be preferable even to do without the gauge and to use the instrument in its simplest form, as represented in Fig. 1. The operator will soon learn from observation of the way in which the drops fall down, when the exhaustion is completed. Without the auxiliary air-pump, the exhaustion of a receiver of the capacity of about half a litre will take from 20 minutes to half an hour. Though this may appear to be a long time, I have no doubt this method will be found after all, the quickest and simplest, for producing a vacuum as nearly perfect as I have been able to produce.

The slowness of the action is obviously due to the smallness of the bore of the fall-tube. As soon as the calibre of this tube is increased, the time of the operation rapidly decreases: for the contents of two cylinders of the same height are to each other as the squares of their radii, and the time of the operation ought to decrease in the inverse ratio. The proper size of the bore of the fall-tube is $2\frac{1}{2}$ to $2\frac{3}{4}$ millimetres. As soon as I exceeded this

limit, I invariably found the vacua less perfect. It is not difficult with these wider tubes to raise the mercury in the gauge to the height of the barometric pressure, minus 1 or even ½ millimetre; but I have not been able to obtain with them vacua so near perfection as I have been enabled to obtain by the use of fall-tubes of 2½ millimetres calibre. The explanation of this fact must be sought for in the size of the drops, which, as it appears to me, must, in falling down, exercise a certain pressure against the side of the tube thereby preventing the denser air underneath the drop from finding its way again to the part of the tube above the drop, where the air is more rarefied. I have not obtained better vacua by the use of fall-tubes of a calibre less than 2½ millimetres.

Before I proceeded to test the efficiency of the instrument, I directed my whole attention to the construction of air-tight joints; in this, however, I did not succeed. It is a well-known fact, that barometers become inaccurate in time, as air finds its way into the Toricellian vacuum between the glass and the mercury enclosed in it. The vacuum in my instrument is of course exposed to the same sources of imperfection. (To offer a greater resistance to the air, which might enter from the funnel, I have given to the tube *zyo* the form of a U tube.) Leakage, however, happens in a far less degree from this cause, than from the imperfection of the caoutchouc joints. Among the numerous modifications I have tried, I consider the one which I have before described, as the most practicable. With this joint the mercury in the gauge does not sink more than about ½ millimetre in 24 hours. Williamson and Russell,* in constructing their admirable apparatus for the analysis of gases, have met with the same difficulty, and I am able to corroborate their statements. The porosity of solid bodies is astonishing, and one is almost compelled to think that glass vessels are the only ones impenetrable to gases.

The following degrees of exhaustion have been made with cold mercury, which had merely been filtered through paper to free it from visible impurities, but which had neither been dried nor freed from air by special means. I have worked with heated mercury (100 to 150°C.), but have not noticed much difference in the perfection of the vacua. Even if some slight advantage could be obtained by it, its use would be objectionable, practically speaking, from the risk of endangering the health of the

* Chem. Soc. J. [2], ii, 238.

operator. When the mercury is heated and allowed to run down quickly, the instrument is at the same time converted into a sort of electric machine. In the dark, flashes of electric discharge are seen to light up the exhausted tubes, and sparks may be drawn at intervals from the basin in which the mercury collects, as from an electrophorus. The fall-tube invariably becomes soiled after some time by some impurity in the mercury, and particularly after the employment of heated mercury. I attribute this to the oxidation of the mercury, arising from this electric action, which must be favourable to the formation of ozone. I have to mention, that to attain high vacua, the fall-tube must be clean as well as the mercury.

The length of the fall-tube in the instrument before us is calculated for the use of a liquid having the specific gravity of mercury. Of course, as the specific gravity of the liquid employed becomes less, the fall-tube must be longer. Practically, however, water is the only liquid that need be considered in place of mercury, and I have no doubt that an instrument adapted for water would furnish a simple and most efficient exhausting machine. It is not unlikely that such an instrument might possess advantages which air-pumps of other constructions have not, particularly in hilly countries, where the large volume of a natural waterfall might be rendered available.

I now come to consider the way in which this instrument acts. It is obvious, that it stands in a near relation to the *Trompe* or *Catalonian bellows*, the old and well-known contrivance for producing a blast. My instrument is merely the reverse of the trompe, with this addition, that the supply of air is limited, while that in the trompe is unlimited. The theory which explains the action of the trompe, will at the same time explain the action of my instrument. The theory of the trompe has repeatedly been treated by distinguished philosophers, as Venturi, Magnus, Buff, and others. It would lead me too far to enter upon a criticism of their opinions, which appear to me partly erroneous, partly not to the point. In my opinion, the action of both instruments may, in all cases, be satisfactorily deduced from Kepler's law of the uniformly accelerated motion of bodies. When the clamp z is opened, only a certain and almost uniform quantity of mercury (or any other liquid) can pass at a given time. As soon as a particle of mercury has arrived at x, it is under the influence of the general law of gravitation. It must sink and move with uniformly accelerated

velocity. The same may be said of the second or third particle of mercury; but while the second one is starting, the first one has accomplished a portion of its way, and when the third is starting the distances between one and two and two and three are not equal, but unequal. A vacuum must, therefore, have been formed between them, and hence the tendency of the air to restore the disturbed equilibrium, *i.e.*, by rushing in, if the instrument is open, or by expanding, if a receiver is attached. If the tube into which the liquid runs is larger than the column of liquid which the atmospheric pressure can support, the air in the receiver will of course expand to its last degree. If the mercury is allowed to fall down in *c d* in drops, it will act in exactly the same manner as the piston in a common air-pump. These drops are, so to speak, liquid pistons.

The chief excellence of this instrument appears to me to be its simplicity and the great perfection with which it performs its work. To ascertain the degree of exhaustion, I had at first to resort to a comparison with the barometer but I have not been able to make a barometer, in which the mercurial column stood higher than in the gauge of my instrument, though the barometers were constructed with care, and the readings made by means of a cathetometer. Though my instrument was not air-tight, and consequently not perfect, this apparent equality of the levels in the gauge and in the barometer, is easily accounted for, upon reflection, by the fact that the human eye is not able to distinguish between $\frac{1}{10000}$, or even $\frac{1}{1000}$ part of a millimetre. But being curious to see how much the instrument, even in its present imperfect state, can do, I have taken particular pains to ascertain it; I have tried different ways, but I will describe only that which appears to be the best and most efficient. It is simply the application of Dumas' method for the determination of vapour-densities. I took a receiver of the form *R* (Fig. 2), a bulb extended on both sides into a capillary tube, one of which was open and attached to the instrument, while a portion of the other was broken off and the aperture sealed. The part taken off, and having consequently the same calibre as the portion left attached to *R*, was preserved. The receiver was now exhausted and taken off by sealing it at *A*. This point was broken under the mercury which had just run through the instrument. I did this to meet the objection, that boiled mercury might absorb the remainder of the air in *R*, while, on the other hand, mercury containing more air

might give off some of it and allow it to enter the vacuum. If, now, the receiver had been perfectly exhausted, the mercury would have filled it completely. This however was not the case, a very small air-bubble always remaining at the end of the sealed capillary tube. The capillary tube was broken off at *f*, and the mercury contained in *R* was collected and weighed. Into the capillary tube, first broken off from the receiver, I now introduced by suction a small particle of mercury of exactly the same length as the particle of air in *f*. This mercury was then placed in a delicate balance and weighed. The weight of this particle of mercury bears the same proportion to the weight of mercury in *R* as the weight and volume of air remaining in *R*, after exhaustion, bears to the weight and volume of air in *R* before exhaustion. The highest proportion I have attained in this way is $\frac{1}{1300000}$, and upon the average I consider it not a difficult thing, with the present means, to exhaust a receiver to $\frac{1}{100000}$. From this it is obvious that a barometer may be made by simply exhausting and sealing a tube, one end of which is then broken under mercury. I have actually made some in this way.

I have applied the finest reaction for the presence of gases, viz., the absence of any electric discharge in a perfect vacuum.* The few tubes I have made hitherto always showed a slight discharge, which, however, I have chiefly attributed to the presence of mercurial vapour, though I could have ascertained it by means of spectrum analysis. I have tried to remove this vapour by introducing, between the instrument and the electrical tube, a tube exposed to a cold of – 10° C., or filled with finely divided gold or freshly ignited charcoal, but the intensity of the whitish-green electric light appeared to be not much diminished by these means. From this I infer that the mercurial vapour has either not been condensed, or the supporter of light is due to another body. Being aware of the subtlety these experiments require, and of my shortcomings in their performance, I should not like to say more about them now, but I hope to repeat and study them with care hereafter. At any rate, I have learned this much, that during the exhaustion with my instrument, the colours of the electric discharge change from intense red and blue to faint white and green; that I have passed the limit at which the density of the air is most favourable to the electric discharge; that the stratifications are exhibited in an admirable

* Gassiot, Phil. Trans., 1858-9.

manner; and that the instrument will prove useful for the performance and study of these experiments, which on account of their beauty have excited so large an interest.

Before concluding this paper, I should like to say one word more about the theory of the action of the instrument. Is the action entirely due to the accelerated velocity of the mercury and the elasticity of the air? I answer, yes. Struck by the extraordinary attenuation of the air, and misled by Venturi's theory, I was at first much inclined to attribute the action partly to two other agencies: the attraction of gases to liquids, and their absorption by liquids. But the following experiments showed me that I was mistaken. I forced water through short *T*-pieces at different velocities, using from a slight pressure up to that of several atmospheres, and I have not been able to raise water in a tube connected with the other branch of the *T*-piece to a greater height than that corresponding to the length of the tube from which the water was expelled. But this does not show so much as the fact, that when the calibre of the fall-tube is larger than $2\frac{1}{2}$ millimetres, it is impossible to raise the mercury in the gauge so high as it stands in the barometer, however long the mercury may be allowed to run, and whatever quantity may be used. This shows that the action is entirely mechanical, that the air expands and is cut off, portion by portion, by the falling drops of mercury, and that when the air is highly attenuated, these drops must entirely fill the tube, and even exercise a slight pressure against the sides of the fall-tube, otherwise the action will cease, as in a common air-pump, through the non-action of the valves.

I am under the impression that the use of better materials, and the application of greater skill than I have hitherto employed, will be followed by still better results, and will not improbably furnish instruments capable of producing vacua perfect to our senses; and even if we should not succeed in making a perfectly air-tight joint, the end will still be attained, if we can only succeed in carrying off the air more quickly than it can enter. At any rate, the immense elasticity of air is here displayed in a striking manner, and there is a very wide interval between the attenuation of 1,300,000, to the density of gases which must exist in the powder-chambers of cannons or mines at the moment of explosion. Another striking fact is that exhaustion of $\frac{1}{10000000}$ has been made with cold common mercury, doubtless containing a considerable quantity of air and moisture, which one would expect to be set free

and enter the vacuum as soon as the mercury so violently agitated passes along the fall-tube. But the particles of these absorbed gases, which are set free on boiling, must, at common temperatures, be so intimately connected with the mercury, that their expanding or gaseous properties are lost, as in the oxygen of oxide of mercury.

The main fact which I have established in this paper may be shortly stated to be that, *if a liquid be allowed to run down a tube, to the upper part of which a receiver is attached by means of a lateral tube, and if the height at which the receiver is attached be not less than that of the column of the liquid which can be supported by the atmospheric pressure, a vacuum will be formed in the receiver,* minus *the tension of the liquid employed.*

The properties of highly rarefied gases, and the conditions of that remarkable space in which there is *nothing*, have hitherto been scantily examined, though this subject is suggestive of interesting questions, the solution of which I hope to treat of in my further investigations that border on the, so to speak, negative side of natural philosophy.

The above experiments* were performed in the laboratory of St. Bartholomew's Hospital, and I am glad to have the opportunity of acknowledging most gratefully the facilities which have been offered to me by Dr. Odling in the prosecution of them.

The instrument may be seen at Elliott Brothers, Strand, London, from whom it may be obtained.

IV.—*On a New Reaction for the Production of Anhydrides and Ethers.*

By John Broughton, B. Sc., Chemical Assistant, Royal Institution.

The reactions which are employed for the preparation of the anhydrides of the monobasic organic acids are those originally discovered by Gerhardt, where either the chloride of an electronegative radicle is made to act on the corresponding alkaline salt, giving rise to the production of an alkaline chloride and the anhydride; or the same decomposition is indirectly superinduced

* Communicated to the Chemical Society, June 16th, 1864.

by allowing the pentachloride or terchloride of phosphorus to act on the alkaline salt.

These methods, therefore, essentially consist rather in an almost synthetical formation of the anhydride by a process of double decomposition, analogous in its nature to those by which the compound and double ethers are produced, than in a direct elimination of the anhydride from the salt, of which the reactions for producing nitric and carbonic anhydrides afford familiar instances.

In addition to the above methods, is that described by Gal (*Compt. rend.* lvi., 360), who, by acting on caustic lime and baryta with the chlorides of acetyl and benzoyl, obtained the corresponding anhydrides. As this method obviously necessitates the employment of the chloride of phosphorus, its principle rests mainly on the same decomposition as that discovered by Gerhardt.

It was therefore thought that a reaction by which the anhydrides of the organic acids could be more directly eliminated from salts, in the same manner as some inorganic anhydrides, would possess considerable interest, both in a practical and in a theoretical point of view.

For this purpose, several attempts were made to procure acetic and benzoic anhydrides by the action of boracic acid on the potassium-salts of these acids ; but this method, as might probably have been foreseen, failed to produce the desired substances.

It then occurred to me to try the effect of bisulphide of carbon. This substance was shown by Frémy, many years ago, to be readily decomposed by heated metallic oxides, into carbonic anhydride and a metallic sulphide, and also when heated with water to a high temperature, to form sulphuretted hydrogen and carbonic anhydride (Schlagdenhauffen, *J. Pharm.* [3], xxix. 491). It was therefore thought probable that, by acting on the dry metallic salts of the organic acids with bisulphide of carbon, the metal would be converted into sulphide, and the anhydride set free. With this view the following experiments were performed :—

Crystallised acetate of lead was dried for several hours, at about 120°C., and reduced to as fine a state of division as possible, and a small quantity was placed in a strong glass tube, which was then one-third filled with dry bisulphide of carbon, sealed, and heated in an oil-bath to about 150°C. After an hour's heating, the contents of the tube had become quite black, and after a few hours' exposure, the tube was removed from the bath, allowed to

cool, and then opened, when a violent escape of gas took place, attended with a strong, pungent, acid smell. This gas, on being allowed to pass into baryta-water, was found to be carbonic anhydride. Several strong tubes of hard glass were then charged with 20 grammes each of dry acetate of lead, and as much bisulphide of carbon added as was necessary to make, on agitation with the acetate, a mixture of a creamy consistency. The tubes being then rather more than one-third full, were sealed and heated in the oil-bath, to a temperature of 165°C. The mixture quickly assumed a black colour, and after some hours' heating, one of the tubes, by exploding with great violence, gave warning that a large amount of gas had been liberated. After this it was found advisable to open the tubes once a day, in order to let the carbonic acid escape; and with this precaution the digestion was continued, till it was found that on opening the tubes, only a slight rush of gas took place. The reaction was then judged to have practically terminated.

The liquid contents of the tubes were then poured off as far as possible, and the remainder adhering to the solid sulphide of lead was separated by distillation at a moderately high temperature, and the whole fluid product thus obtained was submitted to distillation. The first product passing over was the excess of bisulphide used, after which the temperature of the boiling liquid gradually rose, when some acetic acid, with a trace of acetone, made its appearance, till the temperature gradually rose to 137°C., and remained constant till the whole had passed over.

The portions of distillate collected near the latter temperature had a pungent acid odour, attacking the eyes and nostrils; when mixed with water, it sank, and gradually dissolved, with rise of temperature. On mixing it with alcohol, the odour of acetic ether was produced. To decide the matter, an analysis was made of the portions which boiled at 137°.

0·3010 grm. burnt with oxide of copper and oxygen, gave 0·5170 of CO_2, and 0·1636 of water.

		Calculated.	Found.
C_4	48	47·05	46·84
H_6	6	5·88	6·03
O_3	48	47·07	—
	102	100·00	

The liquid was therefore acetic anhydride, and its production can be expressed by the equation—

$$2\left[\begin{matrix}C_2H_3O\\ Pb''\\ C_2H_3O\end{matrix}\right\}O\Big] + CS_2 = 2PbS + CO_2 + 2\left[\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O\Big]$$

Experiments with acetate of silver gave a similar result, with even greater readiness.

The above reaction of bisulphide of carbon, it will be perceived, is susceptible of at least three important applications for the formation of organic bodies, if it prove to be in any respect a general one.

1. The production of anhydrides as above from metallic salts.
2. The formation of compound ethers, by allowing the anhydrides in the nascent state to react on an alcohol.
3. In certain cases, for the isolation of anhydrides of electropositive radicles, or ethers.

For the second application it was proposed to produce an ether of acetic acid which had not hitherto been successfully prepared, and for this purpose acetate of phenyl was chosen. This substance Scrugham (*Chem. Soc. Qu. J.* vii., 241) attempted to procure by acting on acetate of potash with an alcoholic solution of phosphate of phenyl, but did not succeed in obtaining it pure. Berthelot had found, during his experiments on etherification, that a small percentage of acetic acid entered into combination with phenylic alcohol when heated with the latter in sealed tubes.

In order to procure this ether, acetate of lead was at first sealed up with an equivalent quantity of phenylic alcohol and an excess of bisulphide of carbon; but after some experiments it was found better to operate with only half an equivalent of phenylic alcohol, as the presence of some of the latter in an uncombined state seriously affected the eventual separation of the acetate in a state of purity. The following was therefore the method adopted:—

20 grammes of well-dried and finely-divided acetate of lead was sealed up in strong tubes, with 3 grammes of phenylic alcohol, and a considerable excess of bisulphide, and heated in an oil-bath to about 170°C. The reaction soon commenced, and proceeded with more regularity than in the preparation of the anhydride, since the lead-salt is soluble in the alcohol, so that the bisulphide is enabled to act with greater readiness. It was found necessary to open the tube daily, for it was shown by some explosions that the pressure

of the liberated gas was very high. When the action had ceased, the liquid products were separated as above described, and redistilled. After the excess of bisulphide had distilled, acetic acid in considerable quantity passed into the receiver, then a small quantity of acetic anhydride, after which the temperature rose rapidly to 190° C., when a liquid of a pleasant empyreumatic odour made its appearance, and when the temperature had attained 210° C. the whole had passed over.

The portions distilling above 190° were rectified, and by repeated fractioning, the greater part was obtained of a constant boiling point of 200°. This was submitted to analysis as follows, by combustion with oxide of copper and oxygen :—

I. 0·2142 grammes gave ·5554 CO_2 and ·1133 H_2O.
II. 0·1964 grammes gave ·5098 CO_2 and ·1060 H_2O.

		Calculated.	I.	II.
C_8	96	70·59	70·71	70·78
H_8	8	5·88	5·87	5·99
O_2	32	23·53	—	—
	136	100·00		

The vapour-density of the liquid was taken as follows, by Gay Lussac's method, using a bath of spermaceti :—

Weight of liquid employed 0·2299 grm.

Observed volume of vapour 70·28 cc.

Temperature 218° C.

Height of barometer 744·5 mm.

Difference of heights of internal and external mercury 32 mm.

Height of column of spermaceti 230 mm. at 45°.

These data give sp. gr. of vapour 4·72. The calculated density of acetate of phenyl is 4·59.

The liquid therefore was acetate of phenyl.

Acetate of phenyl is a colourless liquid, boiling at 200°C., of a peculiar and fragrant odour, which is very persistent; its sp. gr. is 1·074, being somewhat heavier than phenylic alcohol, as acetic ether is heavier than ordinary alcohol. Though quite colourless when freshly distilled, it becomes somewhat yellow by keeping. It is slightly soluble in water, in which it sinks, and to which it imparts its peculiar odour. It is neutral to test-paper, and is not decomposed by boiling water; even when heated with water to 180°

it acquires but a very slight acid reaction. Boiling solutions of the fixed alkalis gradually dissolve acetate of phenyl, with formation of an alkaline acetate and phenate. Its index of refraction is the same as that of German fusible glass, on which account tubes of the latter become invisible when immersed in this ether.

It will appear from the above experiments that this reaction of bisulphide of carbon will most probably be found of service in isolating anhydrous acids, in cases where the ordinary methods are not convenient, and will also, it is believed, receive many applications as a general mode of preparing compound ethers, since it has the advantage of being applicable to small quantities. Phenylic alcohol, which has hitherto been found so difficult of etherification, may probably, by the above process, yield its full complement of ethers in the manner of alcohols of other series.

Experiments have been commenced to illustrate the third application of this reaction, namely, that of eliminating phenylic ether from phenate of lead.

Whether the method be applicable as a means of procuring double ethers and anhydrides, further experiment must show.

In conclusion, the following desultory qualitative experiments have been tried:—

Chloride, bromide, iodide, and fluoride of lead are not attacked by bisulphide of carbon.

Nitrate of silver is most readily acted on by bisulphide of carbon, with production, in addition to sulphide of silver, of a green liquid and a white solid substance; but on attempting to open the tubes, they have burst with a most violent explosion.

Sulphate of lead is not affected by sulphide of carbon.

Benzoate, succinate, and ferrocyanide of lead are readily acted on by the bisulphide.

Formate of lead is entirely converted into sulphide by bisulphide of carbon, with much evolution of gas; traces of a strong acid are evolved, together with a sulphur-compound of a powerful odour; all attempts to obtain formic anhydride have been unsuccessful, the latter being apparently entirely decomposed into gases.

Oxalate of lead is entirely unaffected by sulphide of carbon at a high temperature.

I take this opportunity of expressing my thanks to Professor Frankland for opportunity and leisure to make the above experiments.

V.—*Laboratory Memoranda.*

By Robert Warington, Junr., Assistant to Professor of Chemistry, R. A. College, Cirencester.

I. *The Action of Ferricyanide of Potassium upon Ferric Salts.*—Most works on chemistry describe this reaction as producing a "dark-brown," or "reddish-brown" fluid, and state that no precipitate is formed;* some Manuals, however, tell us that a "greenish," or even a "dark-green" liquid is the result.† These statements are all incomplete, and may possibly mislead.

First, as to the colour. The dark-brown liquid is produced only when the ferricyanide of potassium is in *excess* of the ferric salt; the tint in this case is a dark sherry-brown. When the proportions are reversed, and a drop or two only of the ferricyanide mixed with an excess of ferric chloride, a brilliant emerald-green tint of a slightly bluish tinge is the result. If the proportion of ferricyanide of potassium is then gradually increased, the colour is first changed to sap-green, then olive-brown, and at last reaches the dark sherry tint before described. The whole series of colours is well seen if a single drop of ferricyanide of potassium is allowed to run down the side of a test-tube half filled with dilute ferric chloride; a brown ring forms at the surface, where the ferricyanide is in excess, from which streaks of colour slowly descend, their tint changing from brown to bright green, as they fall further towards the bottom.

It appears, then, that the colour produced on mixing an alkaline ferricyanide and a ferric salt is essentially dependent on the proportion of each which may be present.

Lastly, as to the statement that the liquid remains *clear*. This is true only when the solution is sufficiently acid; *basic* ferric salts afford an immediate pale brown precipitate with ferricyanide of potassium.

These results were all obtained with a freshly prepared solution of the ferricyanide.

II. *The Solubility of Magnesia in Alkaline Salts.*—That magnesia dissolves in salts of ammonium, with evolution of free ammonia, is a sufficiently familiar fact. That the presence of ammonium-salts hinders or entirely prevents the precipitation of hydrated magnesia by an alkali, is equally well known; but it is not, per-

* So Rose, Fresenius, and Gmelin.

† Thus Miller, and Northcote and Church.

haps, so generally understood, that salts of potassium and sodium have an exactly similar effect, though in a far smaller degree. The action of ammonium-salts, in preventing the precipitation of magnesia, is usually explained as owing to the formation of double salts of magnesium and ammonium. If this theory be correct, then the presence of *any* soluble base forming double compounds with magnesium, ought to have a similar effect, and consequently we should expect that salts of potassium and sodium would in this particular behave like salts of ammonium.

Magnesia dissolves to a small extent in a strong solution of a salt of potassium, and also in salts of sodium, the alkaline salt being in this case evidently decomposed, as the liquid strongly reddens turmeric paper.

The following experiments were made as to the faculty of alkaline salts to prevent the precipitation of hydrated magnesia. Two equal volumes of a solution of chloride of magnesium were taken; in one of these 200 grs. of chloride of potassium were dissolved; both were then treated with equal volumes of a solution of caustic potash; and, after standing some hours in a warm place, filtered, and the magnesium in the filtrate (that, therefore, which the potash had *failed* to precipitate) estimated by phosphate of sodium in the usual way. The experiment with chloride of potassium yielded 1·54 grs. of $Mg_4P_2O_7$, the other only 1·39 grs.; the potassium-salt had clearly then to a slight extent prevented the precipitation of magnesia. An experiment with chloride of sodium yielded a similar result. Trial was also made with sulphate of magnesium, the sulphates of potassium and sodium being added. The amounts of magnesium unprecipitated by the potash are shewn by the following weights of pyrophosphate obtained:—

With sulphate of magnesium alone	·15	grs.
„ „ and sulphate of potassium	·50	„
„ „ and sulphate of sodium ..	·56	„

Another experiment, in which caustic soda was the precipitant, gave similar results.

With sulphate of magnesium alone	·94	grs.
„ „ and sulphate of potassium	1·15	„
„ „ and sulphate of sodium ..	1·35	„

When these experiments were repeated with an increased quantity of caustic potash or soda, the effect here noted practically

disappeared, a trace only of magnesium being found in any filtrate; this indeed took place when the amount of potash was increased by one-half, or even less. The excess of potash doubtless decomposed the double salt first formed, in the same way that a large excess of ammonia precipitates hydrated magnesia, even in the presence of sal-ammoniac.

It appears then that salts of potassium and sodium do really hinder the precipitation of hydrate of magnesium,* though to not nearly the same extent as salts of ammonium; a result which well accords with theory, as the double compounds of magnesium with the former salts are well known to be far less stable than those with the latter.

Another fact in connection with the solubility of magnesia in alkaline salts, is the decomposition of this solution by water under certain conditions For instance, if a strong solution of magnesium be mixed with sal-ammoniac and free ammonia, the proportion of the two latter being so adjusted as *just* to prevent precipitation on standing, the equilibrium of the mixture thus formed is destroyed by the addition of water, and magnesia is precipitated. In one experiment a mixed solution of the chlorides of magnesium and ammonium was treated with twice its volume of the strongest ammonia; at the end of twelve hours, the solution was still perfectly clear. An exactly similar mixture was prepared, and diluted with water to three times its bulk; at the end of twelve hours a considerable precipitate of magnesia had fallen. Salts of ammonium appear then to hinder the precipitation of magnesia in proportion to their concentration.

This fact serves to explain a phenomenon sometimes observed when making determinations of phosphoric acid. If the washings of the phosphate of magnesium and ammonium are allowed to mix with the main filtrate, an opaque ring is often formed at the junction of the two liquids, alarming the operator with the idea that his precipitate is washing through; the washings, however, if collected separately, are found to be perfectly clear. The cause of this appearance is probably the precipitation of the excess of magnesia on diffusion into the wash-water.

* According to Longchamp (Ann. Chim. Phys., [3], xii. 255.) the precipitation of *carbonate of magnesium* is less complete in proportion to the amount of alkaline salts present.

VI.—*Note on the Boiling Points of Isomeric Ethers of the Formula* $C_nH_{2n}O_2$.

By J. Alfred Wanklyn.

From Kopp's paper it would seem that those ethers of the fatty acids which are isomeric with one another, should have the same boiling point, or that all the ethers having the formula $C_nH_{2n}O_2$, in which n has a constant value, have the same boiling point. This proposition and its consequences have found a place in the Handbooks.*

Having had occasion to prepare valerianate of ethyl and acetate of amyl, both of which have the same total formula, viz.,

$$C_7H_{14}O_2,$$

I have observed that there is a considerable difference in their boiling points. Valerianate of ethyl boils at 133° C.; acetate of amyl at 140° C. The boiling point of acetate of amyl was found by Cahours to be 125° C., but it is probable that there was amylic alcohol present in the specimen examined by that chemist. A mixture of acetate of amyl with a good deal of amylic alcohol and a little moisture, would not be distinguishable from pure acetate of amyl by a combustion.

The acetate of amyl which was employed for the determination just given was prepared so as to be free from amylic alcohol. That it was tolerably pure was ascertained by an alkalimetrical analysis.

The natural conclusion from this and a number of facts of a like kind is that Kopp's laws respecting boiling points are not much to be depended on. From the glycols we have learnt that it is not *universally* true that homologous bodies rise in boiling point as they increase in complexity, and a careful examination of almost every homologous series discloses the fact that "the increment" is not uniform in all parts of the same series.

Thus, for instance, iodide of methyl boils at 43° C., iodide of ethyl at 73°, and iodide of amyl at 146° C., giving an increment of 30° for the first addition of CH_2, and an increment of $\frac{73}{3}$° or 24·3° for each CH_2 between ethyl and amyl.

* See Kekulé's "*Lehrbuch der Organischen Chemie*," dritte Lieferung, page 601; also Limpricht's book, page 256, et seq.

Again, zinc-methyl boils at 46° C., zinc-ethyl at 119° C.: difference 73° for CH_2; whilst zinc-amyl boils at 220°C.: difference for CH_2 equals $\frac{1}{3}\frac{0}{1}$ or 33·7°.

There is also the well known example of methylic alcohol which boils at 65° C., instead of at 59° C. or 60°C., as Kopp's theory would require. Higher up in the alcoholic series we encounter Wurtz's isomeric amylic alcohols, having different boiling points, and then the isomeric hexylic alcohols. Although it will be objected that the hydrate of amylene and the β-hexylic alcohol are not true homologues of ethylic alcohol, still the unexpected boiling points of these bodies shows that mere inspection of the molecular formula of an alcohol is very little guide to the boiling point of that alcohol.

VII.—*Note on the Action of Chloropicrin and Chloroform on Acetate of Potash.*

By Henry Bassett.

Although the experiments described in the following short note have not led to the production of any new substance, I venture to think they are of some interest, as a further example of the reactions of these bodies, and as tending to confirm the views as to their constitution arising from the behaviour of their ethylic derivatives; namely, that the groups C and CH contained in them have a decided tendency to form the corresponding carbonic and formic acids, in preference to giving rise to any tetra- or tri-atomic alcohol derivatives.

Chloropicrin heated to 100° in a closed vessel with fused acetate of potash, and alcohol, is decomposed with great readiness. No gas is disengaged, but a considerable quantity of chloride of potassium is formed, and the solution becomes acid. On cooling, a crystalline salt is deposited in large quantity. The experiment was tried at first with four equivalents of the acetate to one of chloropicrin, but it was found that a large quantity of the latter remained unacted upon after twelve hours' heating, although the reaction appeared to be completely finished. The quantity of acetate was therefore increased in subsequent experiments, until,

with nine equivalents of acetate, it was found that very little, if any, chloropicrin remained.

The alcoholic solution was filtered hot from the chloride of potassium, and gave a large crop of needle-shaped crystals on cooling. A further quantity was obtained from the mother-liquor by distilling off the alcohol in the water-bath. In this distillate, which had an acid reaction, the smell of acetic ether was very perceptible. The salt was recrystallized from alcohol, drained, and dried as completely as possible by pressure, and then left over sulphuric acid in vacuo for several hours. The dry salt thus obtained was not nearly so deliquescent as ordinary acetate of potash, and rotated violently on the surface of water. On heating, it gave off a large quantity of acetic acid, and left a fused mass of the normal acetate of potash.

Submitted to analysis, it gave the following results:

1. ·499 grm. evaporated to dryness with hydrochloric acid and ignited, gave ·238 grm. chloride of potassium.
2. ·5065 grm. burnt with chromate of lead gave ·561 grm. carbonic acid and ·213 grm. water—numbers which agree perfectly with the composition of bi-acetate of potash, as will be seen by comparing the percentage amounts:—

	Exper.	$C_4H_7KO_4$
C	30·21	30·38
H	4·67	4·43
K	24·95	24·68
O	40·17	40·51
	100·00	100·00

The reaction taking place is as follows:—

$$CNO_2Cl_3 + 9C_2H_3KO_2 + 3C_2H_6O = 3KCl + KNO_2 + K_2CO_3 + 3C_4H_8O_2 + 3C_4H_7KO_4.$$

Acet ether. Biacet. Potash.

The presence of nitrite and carbonate of potash was distinctly shown by the usual tests in the precipitated chloride of potassium.

Chloroform heated to 100° with acetate of potash and alcohol was only slightly attacked, but at 125° a large quantity of chloride of potassium was formed. In three or four hours the action was

complete, and the solution when cold deposited a large quantity of crystalline salt. On opening the tube, a small quantity of carbonic oxide escaped. After distilling off the alcohol, which smelt of acetic ether, the remaining salt was crystallized and dried, when it presented exactly the characters of that obtained from the chloropicrin experiments, and the identity of the two salts was shown by a potassium estimation.

·4595 grm. gave ·22 grm. chloride of potassium, corresponding to 25·07 p. c. of potassium.

The reaction in this case is perfectly similar to the former one.

$$CHCl_3 + 6C_2H_3KO_2 + 2C_2H_6O = 3KCl + CHKO_2 + 2C_4H_8O_2 + 2C_4H_7KO_4.$$

The formate was readily detected in the salt obtained by evaporation of the mother-liquor from the bi-acetate, by the reduction of bichloride of mercury, and by the evolution of carbonic oxide when warmed with sulphuric acid.

The ease with which chloropicrin is attacked by reagents suggested an experiment with aniline; in fact, on heating a mixture of one part chloropicrin with three of aniline to 145°, and then removing the lamp, a violent reaction is established, accompanied by the evolution of a considerable quantity of nitrogen. Boiling water extracts from the product a certain quantity of a red colouring matter similar to that originally obtained by Hofmann from the tetrachloride of carbon; the solution also contains the hydrochlorate of a solid base, which was purified by precipitation and crystallisation, and converted into a platinum-salt.

·4605 grm. gave ·091 grm. platinum, corresponding to 19·76 p. c. the platinum-salt of carbo-triphenyl-triamine containing 20·01 p. c.

I am at present studying the action of chloropicrin on cyanide of potassium, and anticipate from it some interesting results.

VIII.—*On Microscopical Research in relation to Pharmacy.*

By Henry Deane, F.L.S., and Henry B. Brady, F.L.S.

[Read at the Bath Meeting of the British Pharmaceutical Conference, Sept., 1864.]

We have chosen for the particular subject of the present communication the various preparations of opium. Whether regarded in respect to their importance in the practice of medicine, their variability in strength and character, or the peculiar conditions in which the active matter exists in the crude drug, no better subject could be found for the purpose in view.

Opium, as is well known, is an extremely composite substance, being a pasty mass formed of resinous, gummy, extractive and albuminous matters, containing a larger or smaller percentage of certain active principles diffused through it. These principles are morphine, narcotine (with its two homologues), codeine, narceine, meconine, thebaine, and papaverine, either existing free or in combination with meconic, sulphuric, or other acids, the sum of the crystalline constituents, exclusive of inorganic salts, contained in good samples of the drug, being from twenty to thirty per cent. of its entire weight. Any preparation, exactly to represent opium, must contain the whole of these principles, as indeed the tincture may be said fairly to do.

It has, however, been shown that some of the principles are inert, and others even deleterious in their action, and we have consequently had a class of preparations introduced which are understood to be of superior efficacy, not from their containing any active matter which the tincture does not contain, but because they are free from certain substances which are retained by it. Narceine, meconine, and meconic acid are believed to be inert, whilst narcotine possesses properties widely different from those for which opium is usually employed. Of the bulkier constituents, the resin appears to be worse than useless, whereas the bitter extractive, though opinions differ with regard to its precise properties, seems at any rate to increase the narcotic power of the more active constituents. A typical preparation of opium should therefore at least contain the whole of the morphine and codeine, with meconic or some other acid to keep them in solution, and the bitter extractive. Codeine itself, and the salts of both codeine

and morphine, are readily soluble in either water or alcohol; the remaining principles are fully dissolved by alcohol, but scarcely soluble in water; hence, in the preparations alluded to, water rather than alcohol is used as the solvent.

The process we adopt in examining the constituents of a fluid preparation of this sort under the microscope is a very simple one.

Having, as a preliminary step, taken the specific gravity, and ascertained the percentage of carefully dried extract contained in it, we evaporate a small quantity, usually from four to six drachms, on a sand-bath in a watch-glass, to about the consistence of treacle. It is then poured upon a slip of glass and covered with a piece of thin glass, and after standing a few days, it is sealed in with gold-size. Crystallization sometimes commences before the preparation is removed from the watch-glass, sometimes immediately after transferring to the glass slip, but in many cases not for several days. The time taken is dependent on one of two influences, viz., the quality of the opium, and the exact degree of inspissation.

In determining the value of a preparation from the appearance of this extractive under the microscope, we do not rely entirely upon the amount of crystallization; it is requisite to go one step further to obtain the full value of our labour, and by investigating the form and physical characters of morphine and its compounds, of codeine, narcotine, meconic acid, &c., place ourselves in position to see the significance of the appearance the slide exhibits, and to identify any crystalline principles which may be present. Nevertheless, even in the absence of very accurate knowledge, any one who will make a few experiments for the sake of practice will soon be able, by observing the presence or absence, the abundance or scarcity, of certain forms of crystals easily seen in typical specimens, to pronounce with little hesitation on the quality or genuineness of samples of any of the ordinary preparations of opium.

Before proceeding to speak of the opiates which have come under our examination, it may seem necessary to say a few words on the forms assumed by the various opium principles and the physical characters their crystals present. This, together with certain drawings we have made carefully from specimens, will afford a key to our further remarks.

In the first place:—

Morphine.—The pure alkaloid crystallizes in right-rhombic prisms

often running into needles. The single crystals have but little effect upon the polarized ray, but where the solution has been concentrated (as from alcohol), and the acicular crystals are much overlaid, they present a good deal of colour. (Plate I, fig. 1.)

It is exceedingly difficult to say in what condition morphine exists in opium; we are well aware that it has been set down as meconate, with a smaller percentage of sulphate, but we have reason to suspect that sulphate is present to a larger extent than is generally supposed. The messing and manipulation which all kinds of opium appear to undergo before they reach this country, renders the belief which is suggested by other circumstances, that a portion of the meconic acid is decomposed, extremely probable. It is scarcely likely that a substance which even boiling water decomposes, with evolution of carbonic acid, should remain unchanged through the various treatments to which the drug is subjected.

Meconate of Morphine is set down in chemical works as being uncrystallizable, a statement to be accepted with reservation; for by careful manipulation peculiar conical crystals may be obtained either from the solution of the commercial salt in dilute alcohol (Plate I, fig. 3 *b.a.*), or by the evaporation of mixed solutions of morphine and meconic acid (Plate I, fig. 3 *b.b.*). These crystals do not resemble any that are found on evaporating opium solutions; but as we have said, the subject requires more investigation than we have as yet been able to give to it.

Sulphate of Morphine takes the form of small flat-ended prisms, with a strong tendency to collect in radiating tufts; only the larger flat crystals polarized (Plate I, fig. 3 *a*).

Codeine crystallizes in octahedra running into four-sided prisms. In the octahedral condition it is not easily mistaken for any other of the oplum-alkaloids, but the prisms strongly resemble those of narcotine. (Plate I, fig. 4 *a*).

They may be distinguished by their not presenting the fluted or striated surface which crystals of narcotine have, and by their much less striking effect on the ray of polarized light.

Narcotine occurs in the form of prisms, with oblique one-or two-faced ends. As above stated, the surface of the crystals is fluted or striated, and on pressure they break up into tolerably regular smaller crystals (Plate I, fig. 2). Owing to a sort of composite structure, they have very marked effect on the polarized ray, more striking indeed than any other of the opium principles. Were it not for this property, they would be distinguished with great diffi-

culty from many other crystalline substances which they resemble in form. There is a tendency, as in other cases, to cluster together in more or less radiating tufts, but the individual crystals still keep their shape, and do not degenerate into mere radiating plumose needles, like those of narceine.

Narceine.—As narceine exists in opium in about the same percentage, on the average, as morphine and narcotine, it is of greater consequence in these investigations than it is in a medical point of view, being probably an inert substance. It is readily soluble in alcohol, and slightly so in water, and therefore must exist to considerable extent in most of our preparations. The absolute form of the individual crystals it is impossible to determine, but the masses of delicate, somewhat opaque, silky needles, either radiating from a centre or taking an irregular feathery shape, are very characteristic, and the absence of any effect on a ray of polarized light is a negative property of importance. (Plate I, fig. 6 *a*).

Meconine occurs in six-sided prisms with dihedral summits, and has little, if any, polarizing power. (Plate I, fig. 5 *a*).

Thebaine is readily soluble in alcohol, slightly so in water. From solutions in weak alcohol it crystallizes in beautiful rectangular plates, often associated in tufts more or less radiating from a centre. (Plate I, fig. 4 *b*). It is a most beautiful polarizing object.

Papaverine is present to so trifling an extent that it scarcely requires notice. The little which is dissolved by boiling water crystallizes out again on cooling in minute needles often aggregated in rounded balls, so closely packed as to be quite opaque. The large crystals obtained from the alcoholic solution possess slight polarizing properties (Plate I, fig. 6 *b*).

Meconic Acid.—Although the meconate of morphine in opium is an acid salt, it seems probable that part of the meconic acid is also there in a free state; at any rate, we frequently find it in preparations. As it is soluble in both alcohol and water, preparations are pretty sure to contain whatever quantity does exist in the crude drug, unless it has been removed by chemical means The form of the crystals is primarily a square prism, but we have only seen this in minute examples, and it is very difficult to trace the relationship to this type in the flat, pointed lozenges, somewhat resembling the attenuated forms of uric acid, which generally occur. Even these frequently run into still more strange varietal shapes, whose only resemblance to the lozenge-form exists

in their broad centres and two pointed ends (Plate I, fig. 5 *b*). They all have some effect on the polarized ray. Boiling water decomposes meconic acid; carbonic acid is given off, and comenic acid, a substance we have not yet studied, is formed.

We may now proceed to the practical application of the facts enumerated, and detail the results of the examination of the many preparations which have come under our notice.

Of *Turkey Opium* we have investigated—firstly, the tincture, prepared by ourselves from different samples of opium, as well as specimens procured from certain well-known operative chemists; secondly, the extract; thirdly, the wine; fourthly, the more or less aqueous solutions sold as Liquor Opii Sedativus, Battley's, one or two samples prepared by ourselves, and specimens procured from four well-known firms; and fifthly, certain proprietary opiates, viz., "Black Drop," "Jeremie's Sedative," "Nepenthe," and that sold as "Solution of Bimeconate of Morphia."

We have drawn careful figures of the appearances presented by the whole of these, which will do more than any description towards giving a correct understanding of the facts elicited; at the same time, it may be necessary to draw attention to some matters of importance in connection with them.

Tincture yields, on evaporation, crystals of almost the whole of the opium principles, and we find that, as the spirit volatilizes, the resin is also precipitated in an insoluble form. Our own preparation, from different samples of good opium, is tolerably constant (Plate II, fig. 1 *a* and *b*), and agrees in appearance with a specimen procured from a manufacturing house of some standing (Plate II, fig. 3); but neither are quite so rich in crystalline principles as a sample furnished to us by our friend Mr. Morson (Plate II, fig. 2), which seems to have been prepared from peculiarly fine opium.

Extract shows a much smaller proportion of narcotine crystals, with abundance of morphine salts and tufts of narceine (Plate II, fig. 4). Turkey opium is not rich in codeine, and we suppose that in extract prepared from it this principle is retained diffused through the bitter matter. A specimen of *commercial* extract of opium which we have seen, recently imported from the East, is a very different substance, showing fewer morphine crystals, but a large proportion of codeine (Plate II, fig. 5).

Wine.—The mucilaginous matter of wine very much retards, if it does not entirely prevent, the formation of crystals upon eva-

poration, and consequently we can say but little respecting the appearance presented by the extract obtained from vinous solutions.

Liquor Opii Sedativus.—The striking appearance resulting from the evaporation of Battley's Sedative (Plate III, fig. 1) first drew our attention to the mode of investigation now described. We have examined it frequently, and have always met with the same characters. The slides present an almost opaque mass of crystals of morphine-salts and codeine, with a very small proportion of narcotine (and meconic acid?), and, so far as we have observed, complete absence of resinous matter and narceine. Any one who has studied the microscopic characters of this preparation will readily understand how it has kept its place with the profession. We have necessarily thought much as to its probable mode of preparation, and cannot see any reason to doubt the statement made by Dr. Pereira, on the authority of the late Mr. Battley himself, that spirit and water were the only solvents used in its preparation from Turkey opium. Dr. Christison discredits the statement, on the ground of the comparative absence of meconic acid; but, as we have before said, boiling water is sufficient to decompose that acid, and therefore the argument is not a valid one. Though we have experimented much with a view to preparing a similar liquor, we have not yet arrived at an identical result. Plate III, fig. 2 *a* and *b*, shows two preparations with similar, perhaps nearly equal, sedative properties to the original fluid; but it will be seen they both differ considerably in the crystalline matters they contain. The preparation which gives results most nearly like Battley's of any which we have had opportunity of testing is that made by Mr. Morson, of London (Plate III, fig. 3). Of three other makes which we have examined, one (Plate III, fig. 5) is largely charged with resinous matter, and the proportion of crystalline constituents is so minute that we are satisfied its activity must be very small; another (Plate III, fig. 4) gives a few morphine crystals, a good deal of narcotine, and more narceine; a third (Plate III, fig. 6), is chiefly remarkable for its lack of everything crystalline.

There are certain preparations, to which we must next allude, which give little or no evidence as to the active matters they hold in solution by crystallization on evaporation. As examples, we may instance Vinum Opii, amongst officinal, and Braithwaite's black drop, Nepenthe, and a fluid sold as "Solution of Bimeconate

of Morphia," amongst proprietary formulæ. That there should be exceptional cases in which the reaction with a certain peculiar set of tests is doubtful, is only what might have been expected, and it can scarcely be regarded as a weak point in their application. Scarcely any *chemical* test we use but is open to some contingency of the same sort, but as long as we know the conditions of uncertainty it is no drawback to its employment; it only becomes necessary that these conditions should be investigated, and comparison becomes easy.

We have found that when opium is exhausted, the liquor evaporated to an extract, and this extract redissolved in alcohol, the tendency to crystallize is very much lessened or entirely destroyed. The cause of this we are not yet able to explain with certainty, but may state the fact as one which we have noticed in relation to every sort of opium we have worked upon. It will account for the very sparing indications of crystalline principles from all preparations made by redissolving in alcohol a once-formed extract. The residue not taken up by alcohol in the experiment is readily soluble in water, and contains certain crystalline matters which we have not yet examined sufficiently to report upon. Again, the subacid viscid matter left on evaporating wine prevents crystallization, consequently Vinum Opii gives a clear non-crystalline extract; we believe this also to be the reason why one of the proprietary preparations named yields the same result, as it seems to us to be a mere solution of morphine or one of its salts in wine, and not to be made direct from opium. The well known "black drop" gives no crystals upon evaporation, but in their place a peculiar deposit, consisting of an amorphous, almost opaque fæculence. This is probably owing, in great measure, to viscid matter held in solution, which on evaporation becomes insoluble through some change and is precipitated, carrying down with it the active matter. We know too little of the solvent employed to speak very positively, but if the commonly received theory be true,—that it is made by a fermentation process, in which impure malic acid is concerned,—we can readily understand how viscid organic matter may be present in sufficient quantity to produce the result alluded to.

In addition to the preparations of Turkey opium, we have also had the opportunity of experimenting on small quantities of the Patna, Malwa, and Persian varieties, and all of them present peculiarities of interest. An aqueous extract and a tincture have been

made from each, and from the Patna sort sufficient has remained to make a specimen of liquor.

The most striking fact in connection with the whole of them is the existence of large quantities of codeine. In the extract of Patna opium (Plate IV, fig. 1) it is the chief crystalline constituent, and though the liquor (Plate II, fig. 6) shows abundance of the other opium principles, it evidently owes its narcotic effect much more to codeine than Turkey opium does. We have the experience of an opium-eater on this point; he states that the quantity required to produce the effect is larger, but there is less discomfort in the after effects than with other sorts. Malwa opium (Plate IV, fig. 2 and 5) shows more narcine and narcotine, but in the tincture we have, in addition to a mass of minute crystals, certain larger prisms, which are probably codeine. Persian opium (Plate IV, fig. 3 and 6) also evidently contains a large proportion of narcotine and codeine.

We stated at the commencement that this must be looked upon only as a preliminary research, there remaining many points on which our information is far from complete. In continuing the inquiry we intend to devote ourselves chiefly to the elucidation of certain particulars. *Firstly*, the condition or form of combination in which morphine exists in crude opium; *secondly*, the relation of extract of poppy to opium in respect to crystalline principles; and *thirdly*, the influence which the extractive matters may have in altering the crystals obtained in opium solutions, and the variations of the normal forms induced by this cause.

The general conclusions we have arrived at in addition to a knowledge of the appearances presented by typical and special preparations of Turkey, Patna, Malwa, and Persian opiums are mainly these:—

That tincture, most nearly of any of the preparations, represents the properties, good and bad, of the crude drug.

That when crude opium is taken up with proof spirit as in tincture, the resin separates on evaporation.

That the preparations which have held their ground with the public and the medical profession, in spite of their cost, differ from the tincture in comparative freedom from resin and narcotine, and in containing only a diminished quantity of meconic acid.

That in the preparation of extract of opium it is important to use a large quantity of distilled water to ensure the separation of narcotine and resin.

That when extract of opium is dissolved in water, filtered, and evaporated again to an extract a second or third time, the crystals frequently differ considerably from those seen in the normal or first formed extract.

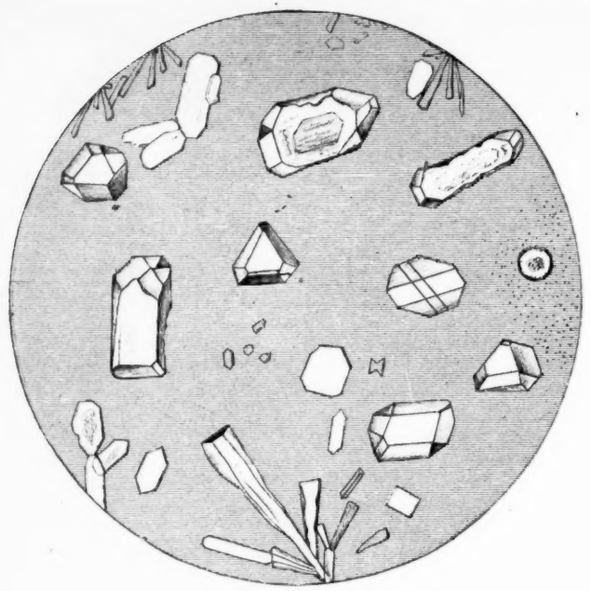
That when extract of opium is taken up with rectified spirit 56° O.P., and evaporated again to an extract, crystallization does not take place, or only to a very trifling extent.

That morphine and its salts, and perhaps other opium principles, do not crystallize readily from their solution in wine.

Finally, it remains for us to express our obligation to our friends Mr. Morson, of London, and Messrs. T. and H. Smith, of London and Edinburgh, for the courteous way in which they have assisted us with specimens, when working upon those of the alkaloids which exist only in minute quantities in opium; without this assistance we could scarcely have procured them in a state of reliable purity.

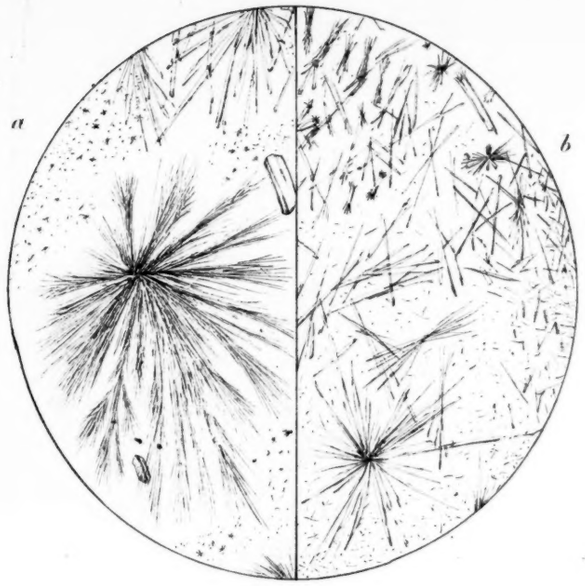
EXTRACTUM OPII.

FIG: 1.



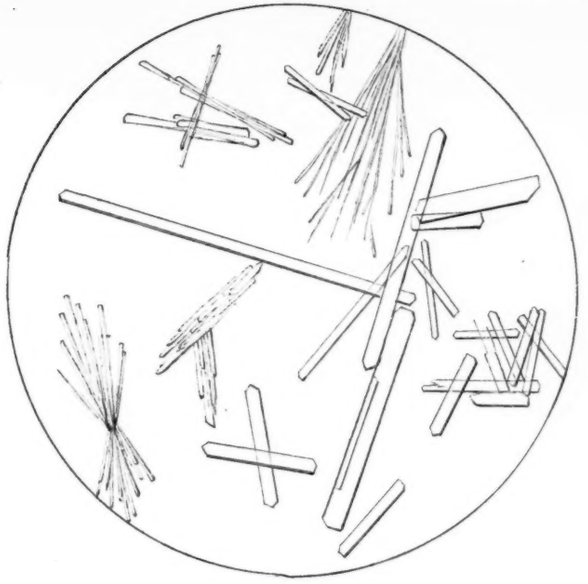
PATNA.

FIG: 2.



MALWA.

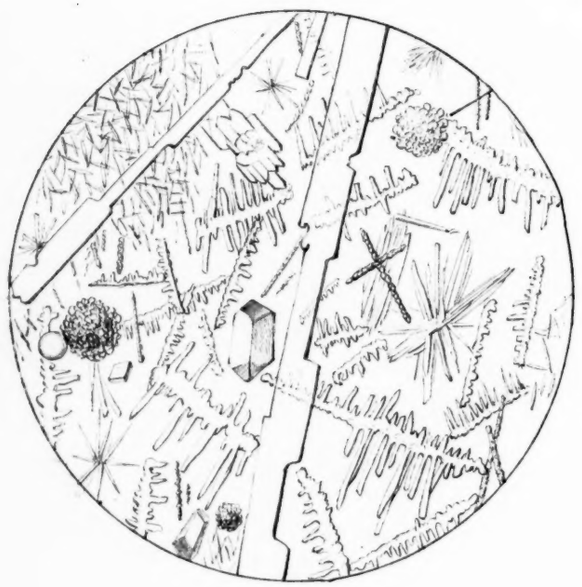
FIG: 3. PLATE 4.



PERSIAN.

TINCTURA OPII.

FIG: 4.



PATNA.

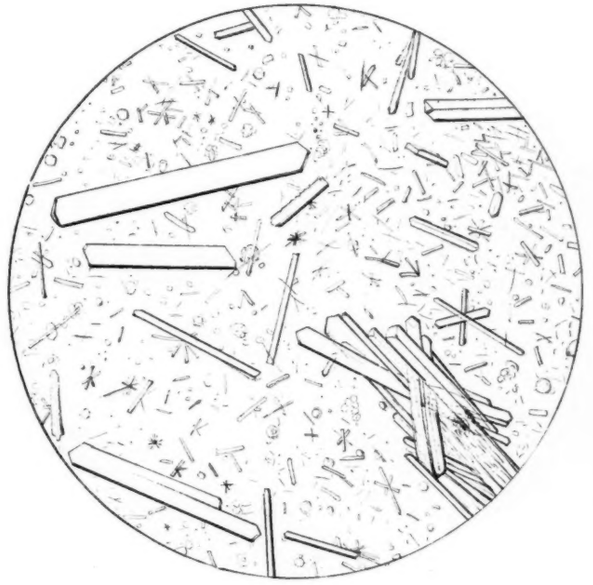
H.B. Brady, del. ad nat.

FIG: 5.

MALWA.

Tuffen West, sculp.

FIG: 6.



PERSIAN.

W. West, imp.

LIQUOR OPII SEDATIVUS.
(TURKEY OPIUM.)

PLATE 3.

FIG: 1.

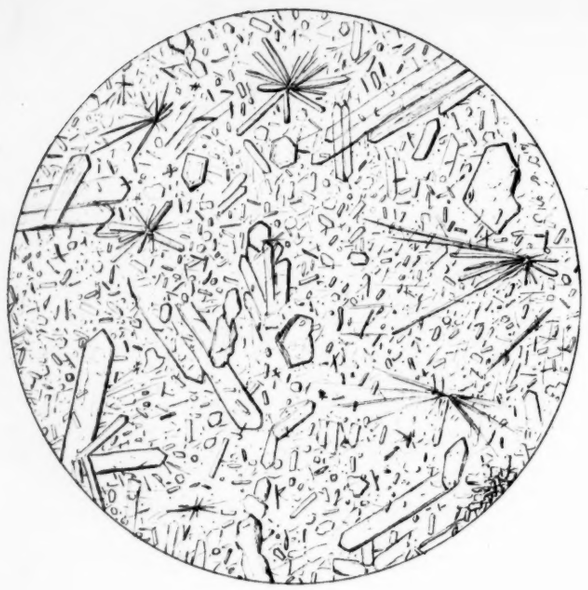


FIG: 2.

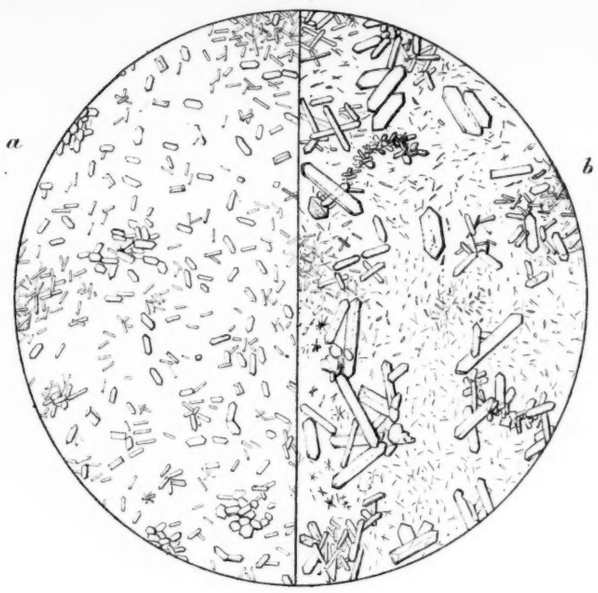


FIG: 3.

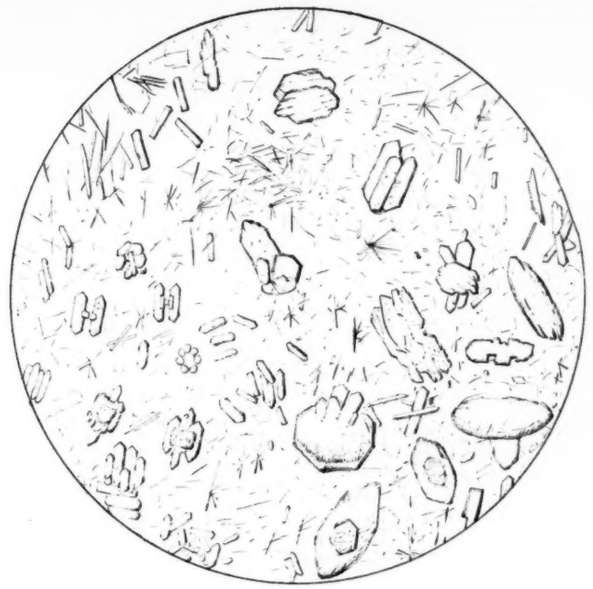


FIG: 4.

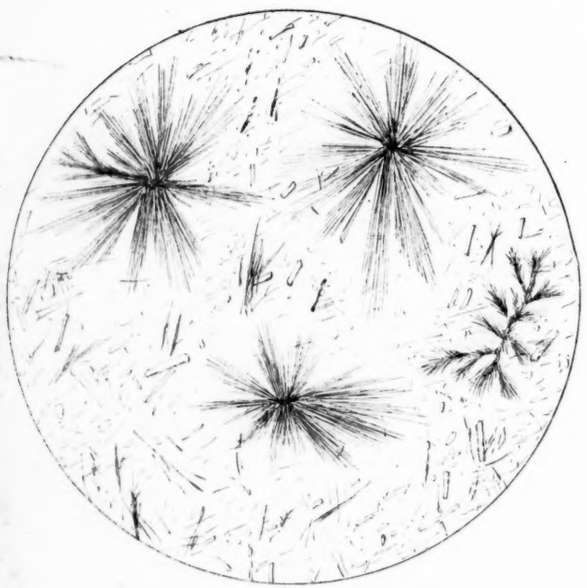


FIG: 5.

FIG: 6.

H.F. Brooke del. et lith.

Tuffen West, sculp.

W. West, imp.

FIG: 1.

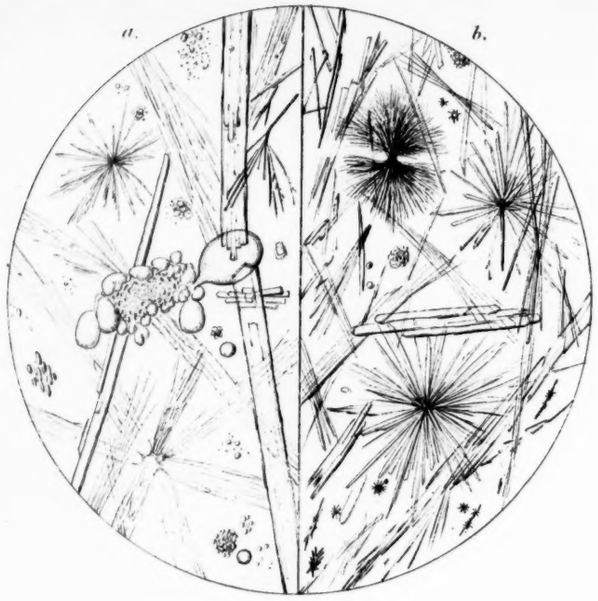


FIG: 2.

FIG: 3.

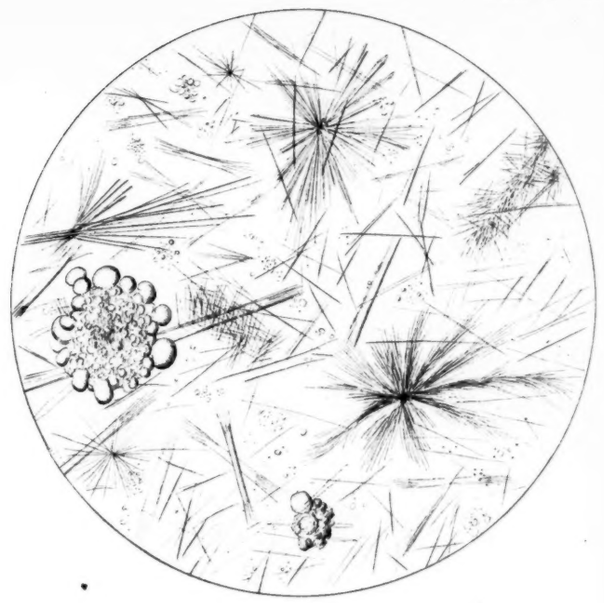
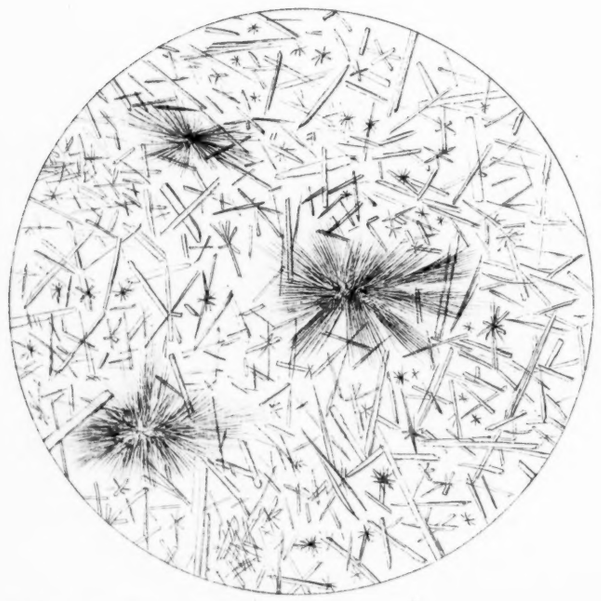


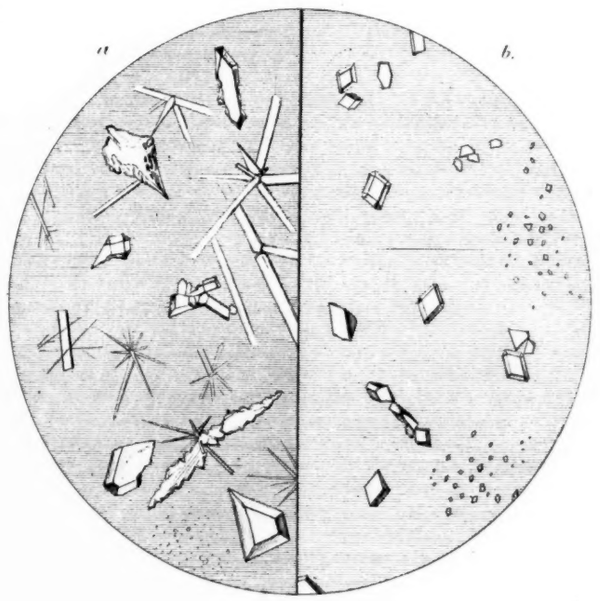
PLATE 2.

FIG: 4.



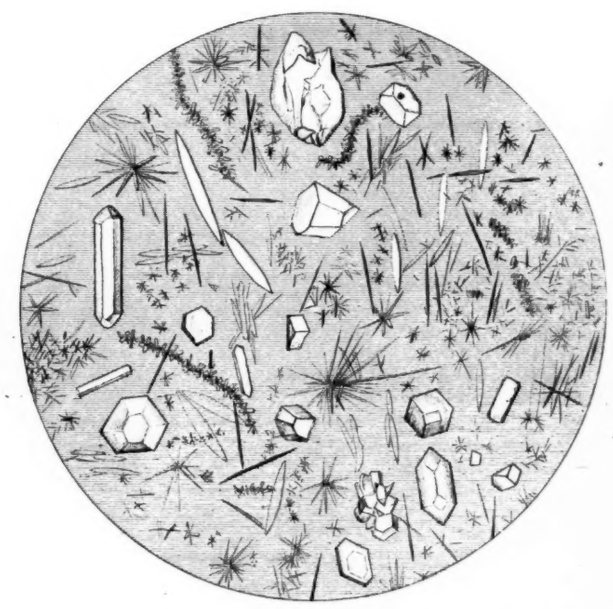
H.B Freely del. et lith.

FIG: 5.



Tuffen West, sculp.

FIG: 6.



T. West, imp.

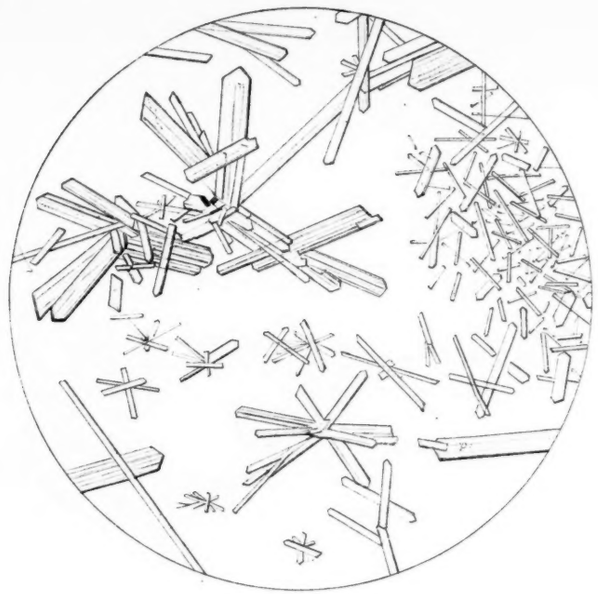
MICROSCOPIC APPEARANCE OF OPIUM PRINCIPLES.

PLATE 1.

FIG: 1.

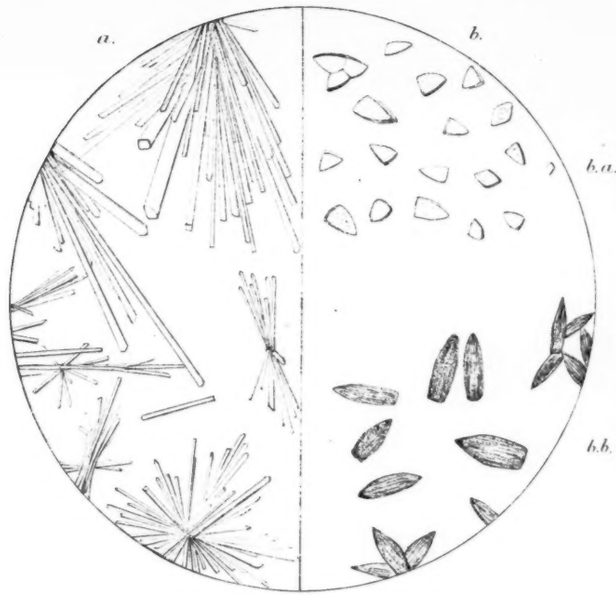
MORPHINE.

FIG: 2.



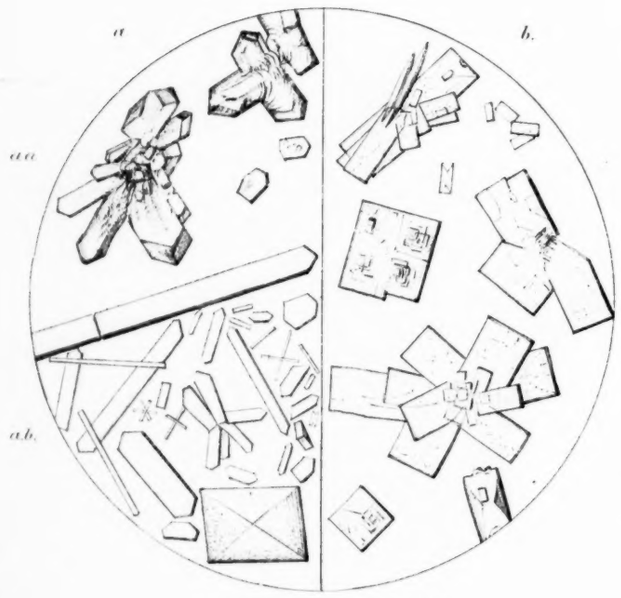
NARCOTINE.

FIG: 3.



SULPH MORPHINE. MECONATE MORPHINE.

FIG: 4



CODEINE. THEBAINE.

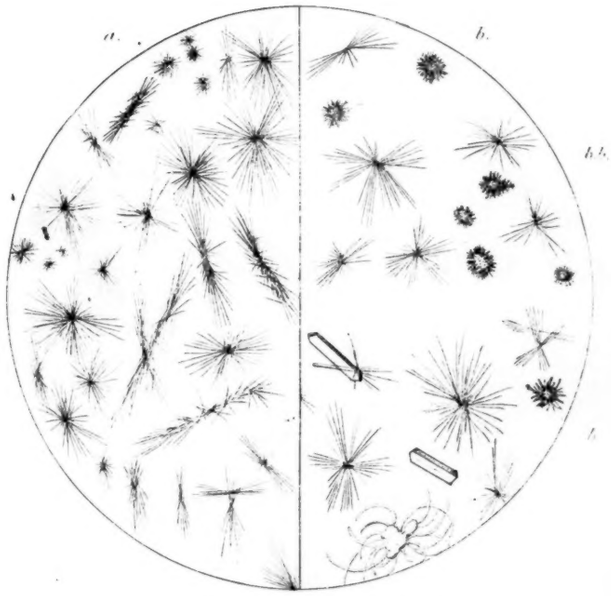
H.B Brady del ad nat.

FIG: 5.

MECONINE. MECONIC ACID.

Tuffen West. sculp.

FIG: 6.



NARCEINE. PAPAVERINE.

EXPLANATION OF PLATES.

Plate I.

Microscopical Appearance of Opium Principles.

Fig. 1. Morphine.
„ 2. Narcotine.
„ 3 *a*. Sulphate of Morphine.
b. Meconate of Morphine.
ba. Commercial salt crystallized from solution in weak alcohol.
bb. Crystallization from mixed solutions of Morphia and Meconic Acid.

Fig. 4 *a*. Codeine.
aa. Crystallized from Alcoholic solution.
ab. Crystallized from Aqueous solution.
b. Thebaine.
„ 5 *a*. Meconine.
b. Meconic Acid.
„ 6 *a*. Narceine.
b. Papaverine.
ba. Crystallized from Alcoholic solution.
bb. Crystallized from Aqueous solution.

Plate II.

Fig. 1. Tinctura Opii (Turkey Opium), prepared by the Authors as standard.
„ 2, 3. Specimens of Tincture alluded to in the text.
„ 4. Extractum Opii (Turkey).
„ 5 *a*. Commercial Extract of Opium, imported.
b. The same, redissolved, filtered, and evaporated.
„ 6. Liquor Opii Sedativus, prepared from Patna Opium.

Plate III.

Liquor Opii Sedativus (Turkey Opium).

Fig. 1. Battley's.
„ 2 *a, b*. Two specimens prepared by the Authors by slightly different processes, from different samples of opium.
„ 3. Mr. Morson's alluded to in the text.
„ 4, 5, 6. Specimens sent out by three operative chemists of standing in London.

Plate IV.

Fig. 1. Extractum Opii, prepared from Patna Opium.
„ 2. „ „ Malwa Opium.
„ 3. „ „ Persian Opium.
„ 4. Tinctura Opii, prepared from Patna Opium.
„ 5. „ „ Malwa Opium.
„ 6. „ „ Persian Opium.

IX.—*On the Oxidation of India Rubber.*

By John Spiller, F.C.S.

About four years ago Dr. A. W. Hofmann communicated to the Chemical Society an interesting research, which treated of the changes that gutta-percha is found to undergo by free exposure to air under the influence of a hot climate, and the author brought forward conclusive evidence to show that the deterioration in quality observed in the coating of the Indian telegraph wires, was to be accounted for by the gradual oxidation of the natural gum.* From a similar point of view I have lately had an excellent opportunity of studying the nature of the changes produced in *caoutchouc* by the operation of like influences. The example to which I beg leave to call attention is one of a very instructive character, and indicates a condition which must be observed in the India-rubber manufacture whenever it is desired to ensure the permanence of an unvulcanized material.

An article is known in commerce under the name of "Patent Waterproof Felt," which is manufactured largely for the purposes of a cheap packing, and is used in the exportation of silk and other valuable fabrics, stationery goods, etc., which are liable to be damaged by water. This material is sold in sheets of great length, and usually about a yard wide; it appears to be made by cementing or matting together the fibres of cotton wool, through the intervention of India-rubber paste or solution, so that after the evaporation of the coal-naphtha, or other solvent, and passing through rollers, a continuous and water-repellent fabric is produced.

About six years ago, I purchased some of this so-called waterproof felt, and made some useful applications of it in the way of photography; some of the material had, however, been laid aside until a few weeks since, when, upon examination, it proved to possess no longer the close structure and waterproof qualities of the original article. It then occurred to me to examine once more the material in the same manner that I had tested it six years ago, viz., by extracting the India-rubber with benzol, and noting the character of the film left upon the evapo-

* Chem. Soc. Qu. J., xiii, 87.

ration of the solvent. The original fabric thus treated furnished a beautifully white cotton flock, and a solution which, being evaporated, left a highly elastic film of pure India-rubber; but these characters are no longer possessed by the fabric examined at this later period. By digesting with benzol the cotton fibres are left in a discoloured condition, and a solution is obtained, which, upon evaporation, yields a resin, or brownish yellow, brittle substance, closely resembling shellac. A considerable quantity of this altered India-rubber has been extracted by solvents, and its properties may be thus characterized :—

It is freely soluble in alcohol, especially if warmed, in chloroform, wood-spirit, and in benzol, as already stated. It is not appreciably soluble in oil of turpentine or bisulphide of carbon, and but sparingly so in ether. In alkaline solutions, both caustic and carbonated, it is freely soluble, and may be again precipitated on neutralising with acids. Like India-rubber itself, it becomes bleached upon immersion in aqueous ammonia. The resin fuses below the temperature of boiling water, and when more strongly heated in a retort, gives off an amber-coloured oil of agreeable aromatic odour, besides furnishing water, a proof of its containing oxygen. At ordinary temperatures it is extremely brittle, and highly electric, so much so that it cannot be powdered in an open mortar without considerable loss. A glass rod coated with the substance exhibits the phenomena of "resinous electricity" when rubbed with silk. The chief examination has been made upon the substance extracted from the fabric by warm alcohol, which leaves insoluble, besides the cotton, a very small proportion of unchanged India-rubber, easily separated by filtration, and the amount of the brittle resin extracted in this manner from a square foot of the fabric weighed, after complete evaporation of the solvent over a water-bath, 74 grains. A quantitative analysis of this substance has been made, and the numbers furnished by combustion with oxide of copper indicate the following percentages, which I have placed in juxtaposition with the figures reported by Dr. Hofmann, for one of his compounds: —

	India rubber. J. S.	Gutta percha. A. W. H.
Carbon	64·00	62·79
Hydrogen	8·46	9·29
Oxygen	27·54	27·92

For the reasons adduced by Dr. Hofmann in the case of the altered gutta-percha examined by him, I abstain from constructing a formula, and merely regard this substance as an oxidation product formed directly from caoutchouc by the absorption of atmospheric oxygen, in much the same manner as resins are formed from essential oils and other hydrocarbons.

X.—*On a Dense Brine, from Saltsprings, Nova Scotia.*

By Prof. How, D.C.L., University of King's College, Windsor, N.S.

The analysis of mineral waters is a subject full of interest. Chemists see in every instance means of comparison respecting the accumulation of ingredients in the solvent, and matter for argument concerning the chemical changes capable of producing the associations observed. The significance of water analyses, when properly executed and reasoned on, is shown by the amount of criticism which has appeared* of late years on the want of uniformity in the modes of arranging the results, both as regards the standard of quantity and the principles upon which allotment of the constituents should be made. Geologists consider the nature and quantity of the contents of waters in connection with the sources of the elements, and find in waters at once the proofs and the agents of important changes in the composition of the earth. Every one will remember what use was made of such evidence in the Presidential address of Sir C. Lyell, at the late meeting of the British Association at Bath. The importance of the researches of Forchhammer, on the constitution of sea-water, has been still more recently declared in the annual address of the President of the Royal Society. Physicians and invalids need only be reminded that curative properties may be at once justly assigned to a water, in consequence of its analysis having been minutely made.

It is curious that among the analyses recorded of late years, few or none are of waters of brine-springs, excepting the very

* See, for examples, R. Haines M.B. in Chemical News, iv, 29 : and Editorials in the same Journal, iii, 285, 315. Also, Miller, ii, 1088 (1st ed.).

valuable series by Hunt, in the "Geology of Canada." Several most interesting waters have been examined, in which chloride of sodium is a chief constituent, but its amount is so nearly approached by that of some other salt, that such waters are properly called strongly saline, in contradistinction to true brines, in which common salt is by very much the preponderating ingredient. I hope the following account of a true brine will be acceptable. The water is remarkably dense, and presents some interesting features in its composition :—

Nova Scotia affords a considerable number of waters, rather strongly charged with mineral matters, springing up in rocks of different geological age. Of these I have described several, and one,* arising at Bras d'Or, in Cape Breton, in rocks probably of silurian age, has, so far as the relative amounts of chlorides and sulphates are concerned, a decided resemblance to that of Wheal Clifford, analysed† by Pro. W. A. Miller, and described by Sir C. Lyell, at Bath. (When I analysed the Bras d'Or water, cæsium and rubidium had not been discovered, and I had only material to determine the leading ingredients.) In both these, and in some similar waters described by Hunt,‡ sulphates are very small in amount; in most of these Canadian waters, indeed, they are absent, while chloride of calcium chiefly abounds with chloride of sodium. Other waters of this province have a large amount of sulphate of lime,§ and exceedingly little chlorine. The water now to be described contains an unusually large quantity of both common salt and sulphate of lime.

The water rises in the carboniferous system, and most probably in the beds called here the gypsiferous limestones. This system is known to furnish brine-springs in various parts of the province, and salt has been made from a few of them, including the subject of this paper. The particular locality of this water has its name from the number of its "salt-springs," for, as I am informed by the Rev. Mr. M'Kay, who occupies the manse at the spot, and who kindly collected the water for my experiments, there are several small salt-springs found here, along a low bank over the length of 150 yards, along which course the salt water oozes out at many intervals, depositing salt at some places. Besides these there are the *principal spring*, from which the water was not

* Chemical News, ix, 97. † Chemical News, x, 181.
‡ Geology of Canada, p. 547. § Chemical News, x, 98, and Trans. N. S. Inst., ii.

taken, for some reason connected with the state of the neighbouring river, and also a spring rising at about 9 yards distance from this in a hole dug by a company who made salt from the water about twenty years ago. From this last spring the water analysed was taken in September, 1864. Mr. M'Kay tells me the water is applied externally, for the cure of rheumatism, and he believes it to be effective. I imagine the spring to be thermal, for my attention was first drawn to it by a gentleman, mentioning as a singular circumstance that the rocks forming the basin of the water in which he bathed were sensibly warm to his feet.

The water as received contained floating organic matter in small amount, and on standing it smelt very decidedly of sulphuretted hydrogen, due of course to the reduction of a sulphate. To obtain an idea of the amount of change occurring under these circumstances, I determined the sulphuric acid twice at an interval of a full month:

The first experiment gave 92·799 grains SO_3 per gallon.
„ second „ „ 91·020 „ „ „

It appears, then, that the waters alter considerably from this cause, which is often observed in operation. On this account the total lime, magnesia, and sulphuric acid given below are as found in portions of the water taken for analysis on the same day; the chlorine was determined four days after. The first alkali determination proving unsuccessful, I could only take that made about a month later than the experiments mentioned, and I found the chloride of potassium to be very small in amount. Phosphoric acid was found in decided, quite determinable, quantity, and I believe the precipitate, formed on by boiling, contained a portion of this acid, for in an analogous water I proved it to be present in the peroxide of iron, obtained from the carbonates thrown down. Boracic acid was also clearly indicated after evaporating about 22,000 grains of water, and testing with turmeric paper, the liquid which drained from the nearly dry residue rendered acid by hydrochloric acid, especially by dipping and drying the paper several times in succession. Bromine was detected without difficulty in about 8,000 grains, but iodine could not be found in the same quantity. Nitric acid could not be found in the residue of 22,000 grains.

The following are the results of the quantitative analysis, so far as it was attempted, the substances actually found being these:—

Grains.			Grains.			Grains in a gallon.
14,000	water	gave by boiling	·755	$CaO.CO_2$	= $CaO.CO_2$	3·775
„	„	„	·775	$2MgO.PO_5$	= $MgO.CO_2$	2·932
„	„	„	·025	Fe_2O_3	= $FeO.CO_2$	0 181
2,500	„	„	·020	SiO_3	= SiO_3	0·560
„	„	„	9·475	$BaO.SO_3$	= SO_3	91·020
„	„	„	5·870	$CaO.CO_2$	= CaO*	89·920
„	„	„	1·280	$2MgO.PO_5$	= MgO†	12·910
300	„	„	44·400	AgCl	= Cl	2561·406
800	„	„	47·240	NaCl	= NaCl	4133·500

By calculating on the plan of Fresenius we obtain, as existing in the water, these constituents :—

	Per cent.	Grains per gallon.
Carbonate of Lime	·00539	3·775
Carbonate of Magnesia	·00418	2·932
Carbonate of Iron	·00025	·181
Silica	·00080	·560
Sulphate of Lime	·22104	154·730
Chloride of Calcium..	·07415	51·910
Chloride of Magnesium	·03904	27·330
Chloride of Sodium (+ a little KCl)	5·90500	4133·500
Phosphoric Acid, Boracic Acid, Bromine, Organic Matter	Undetermined.	
	6·24985	4374·918

Specific gravity at 53° Fah. .. 1046·69.

The total weight of solids contained is very large. The following list shows the contents of some waters selected from the very limited number of those holding more than 1,000 grains in the gallon :—

* After deducting CaO = $CaO.CO_2$ thrown down by boiling.
† After deducting MgO = MgO.COn thrown down by boiling.

	Grains in a gallon.
The most strongly saline water of Cheltenham contains	1033·600*
The strongest *brine* of Canada contains ..	1469·909†
Sea-water (mean quantity) contains	2401·280§
The second strongest *saline* water of Canada contains	3242·260†
The water of saltsprings, Nova Scotia, contains	4374,918
The strongest *saline* water of Canada contains ..	4762,960†
The water of the Dead Sea (largest amount found) contains	18550·000‡

If we compare the Saltsprings-brine and some other waters rich in chlorides with sea water, as regards the relation of chlorine to sulphuric acid, we observe great dissimilarity; thus:—

	Cl.	SO_3.
In the strongest Cheltenham water the relation is as	100 :	32·10
In Sea-water (interior of Baltic) „ „	100 :	14·97‖
„ (open ocean, mean) „ „	100 :	11·89‖
In Saltsprings water „ „	100 :	3·55
In Wheal Clifford „ „	100 :	1·83
In Dead Sea „ „	100 :	0·35

On the other hand, out of 21 Canadian waters abounding in chlorides, sulphuric acid is found in five only, and in these in quite small proportion; and the same is the case in the Bras d'Or water before mentioned as resembling these, and the water of Wheal Clifford. Although the relative amount of sulphuric acid is low in the Saltsprings water, as compared with that in sea-water, the quantity of sulphate of lime it forms is larger than is found in most waters. In looking over numerous analyses, I have met with few waters which resemble closely or exceed the Saltsprings, and some other Nova Scotia waters in this respect. The following

* Scudamore, quoted in Abel and Rowney on Cheltenham Waters, Chem. Soc. Qu. J., 1848, vol. i., p. 193.

† Hunt, Geology of Canada, pp. 547, 548.

§ Forchhammer, Proc. Roy. Soc., in Chemical News, x, 293.

‡ Booth and Muckle, Jahresbericht, 1849, p. 613.

‖ Forchhammer, *loc. cit.*: the other calculations are mine, from published analyses before referred to, except in the case of the Dead Sea; the analysis of this taken is by Marchand, Jahresbericht, 1849, p. 613.

list shows in round numbers the amount of sulphate of lime contained in some of the waters before adverted to, and in some others:—

	Grains in a gallon.
Bras d'Or water, Cape Breton, contains Sulphate of Lime	1
Wheal Clifford water, Cornwall „ „	12
Dead Sea water „ „	61
Bath water „ „	96
Sea water (British Channel) „ „	98
Cheltenham water (strongest) „ „	116
St. Catharine's water, Canada „ „	153
Spa Spring water, Nova Scotia „ „	106
Wilmot water „ „ „ „	122
Saltsprings water „ „ „ „	158
Wilmot water „ „ „ „	161
Ivanda water, The Banat „ „	195

As, according to Fresenius, 70,000 grains of pure water can dissolve only 163 grains of sulphate of lime, it appears that two of the Nova Scotia waters are very nearly saturated, while that of Ivanda in the Banat is considerably supersaturated. Hence we have in the latter case an illustration of the way in which the solubility of salts is modified by the presence of others. The analysis of Ivanda water is contained in an account of some mineral waters, published at the London Exhibition of 1862; it is by Ragsky. It will, perhaps, be agreeable to some to see what other salts are present in the water to account for the presence of so much sulphate of lime; the leading constituents are, in round numbers:—

	Grains in a gallon.
Sulphate of Lime	195
Sulphate of Soda	881
Chloride of Magnesium	109
Nitrate of Magnesia	21
Amount of ingredients being ..	1238

and sulphate of soda is one of the salts mentioned by Fresenius, as increasing the solubility of sulphate of lime. I may mention that in the Spa Spring and Wilmot waters, in the list above

given, the total contents per gallon are respectively, in round numbers, 138 and 141 grains, so that the sulphate of lime is by much the leading ingredient.

While upon the subject of the solubility of salts, I venture to touch upon two other cases, in hopes of exciting useful discussion in an assemblage of chemists. One of these is the solubility of carbonate of lime in water. According to Fresenius (*Quantitative Analysis*, 3rd ed. p. 496), "the simple carbonates of lime and magnesia are not altogether insoluble in water, and, to be as nearly accurate as possible, proper correction must accordingly be made for this in the calculation." On consulting p. 634, at experiment 25, we find that 10,601 parts cold water dissolve 1 part of carbonate of lime; hence a gallon = 70,000 grains of water must dissolve 6·58 grains. Is this amount allowed in all water analyses where the salt is met with? We have only to calculate the results given to find that it is not, though it is found necessary sometimes, when there are not sufficient acids for the bases, to calculate the superfluous bases as carbonates, as is stated to be done in Abel and Rowney's analysis of Cheltenham waters (Chem. Soc. Qu. J. I, 193, 1848), where in one case, 22·08 grains of carbonate of lime are given, while only 12·36 were actually found, per gallon. I observe that at the meeting of the Chemical Society, held February 5th, 1863, this question of the solubility of carbonate of lime was discussed, and it was then stated by Dr. Paul (Chemical News, vii. p. 80), "that experiments of Fresenius and Dr. E. Nicholson prove that about two grains per gallon is the utmost limit of the solubility of carbonate of lime in water." The President, Dr. Hofmann, said, "in his opinion the amount of carbonic acid required to dissolve carbonate of lime was considerably less than that demanded to form bicarbonate of lime; the proportion, however, did not appear to be always definite." Nothing more transpired as to the actual amount of the salt dissolved by water.

The second case is the solubility of carbonate of magnesia in water. To what extent is the salt soluble in pure water? As to its solubility in *mineral* water, Dr. Sterry Hunt says (*Geology of Canada*, p. 557), "It is well known, however, that an excess of carbonic acid is not necessary to retain carbonate of magnesia in solution. Carbonate of magnesia is soluble to a considerable extent in an excess of carbonate of soda or of chloride of magnesium; and a large quantity of magnesia may be held in solution

in the form of sesqui-carbonate." Under these circumstances what becomes of the "proper correction" of Fresenius "for the solubility of carbonates of lime and magnesia in *water*," and what reference can be made to the amount of those salts dissolved, even when water containing them has been boiled to the expulsion of all carbonic acid, if it depends on the nature and quantity of other salts also present.

It was mentioned in a previous page that the Saltsprings water rises in the gypsiferous rocks of lower carboniferous age; it is interesting to find evidence of salt existing in these rocks, as this circumstance, as well as the occurrence of gypsum, makes them resemble the new red of England. As before stated, numerous saltsprings are known to arise in the carboniferous system in different parts of this province, and I may add that at one place, Antigonish, 50 miles from Saltsprings, is the "Salt pond," and at another, Whycogomagh, in Cape Breton, 100 miles from Saltsprings, is the "Salt mountain," supposed to have been so called from the presence of brine-springs. No beds of salt have been met with, but I have small quantities of crystallised rock-salt from a gypsum quarry at Windsor, in which, several years ago,* I proved the existence of sulphate of soda and natro-boro-calcite, and subsequently† of sulphate of soda holding imbedded a new borate, which I called *cryptomorphite*. In this connection the detection of boracic acid in the Saltsprings water, arising some 60 miles from Windsor, has peculiar interest. It is possible that there is a constant association of those substances which have thus already been found together, in greater or smaller quantities in gypsum, or in waters from gypsiferous rocks, viz., common salt, sulphate of soda, magnesia-salts, and boracic acid, with the gypsum forming the enormous deposits of this rock in Nova Scotia. The significance of these bodies occurring together will be seen by consulting Hunt's papers on the formation of gypsum and magnesian rocks (Sill. Am. J. [2] xxviii. 365 et seq.) Beds of limestone rich in magnesia are sometimes found, *e.g.*, at Walton, contiguous to beds of gypsum. Much, however, remains to be learned respecting the relations of these rocks; in the meantime it is well to put upon record such facts as are gathered concerning them.

* Sill. Am. J. [2], xxiv, 230.

† *Ibid.* xxxii, 9, and Edin. New Phil. J., 1861.

XI.—*On the most Volatile Constituents of American Petroleum.*

By Edmund Ronalds, Ph.D.

[From the Transactions of the Royal Society of Edinburgh.]

Crude American petroleum evolves, at ordinary temperatures, a quantity of gas, which takes fire on contact with flame, and, when mixed in certain proportions with air, produces an explosive mixture. It is in consequence of this property that it has been thought necessary to pass a very stringent law, known as the Petroleum Bill, with a view of preventing accidents from the incautious storing and handling of the oil.

The more volatile liquid products obtained by distilling the crude oil are still more highly charged with combustible vapour, which, when these liquids are again distilled, escapes condensation even by the most powerful freezing mixtures.

The liquid constituents of petroleum have now been carefully studied by Messrs. Pelouze and Cahours, and some of them also by Mr. Schorlemmer. These eminent chemists have shown that the oil consists essentially of a mixture of the homologues of marsh gas, having the general formula,

$$C_nH_{2n+1}.\ H.$$

It was during the collection of the more volatile of this series of compounds with a view to their analysis, in which object I have now been forestalled, that my attention was drawn to the large quantities of incondensable gas which escaped at each successive fractionation, and it appeared desirable to ascertain whether the gaseous ingredients of the oil belonged also to the same series, or were accompanied by other hydrocarbons. With this object in view, and still waiting the arrival of some specimens of oil collected and secured in hermetically sealed vessels, direct from the oil-wells, I was enabled, by the kind permission of Mr. Shand of Stirling, to collect the gas which floated over the surface of the crude oil in the barrels in which it is imported into this country. I also obtained from the same manufacturer some of the very first products of the stills employed in refining the petroleum on a manufacturing scale.

The gas floating over the surface of Pennsylvanian oil was collected at a temperature of − 1° C., and was observed to contain

combustible ingredients. It took fire instantly on being brought into contact with flame, burning with a very faint, bluish light, but without explosion. From Canadian petroleum, which is of much thicker consistence, no combustible gas was obtained at that temperature.

The gas was collected over water by simply removing the original wooden bung of the casks and inserting immediately a cork bung furnished with a tube, for the delivery of the gas, and a long shanked funnel tube, through which liquid petroleum was poured.

Thus obtained the gas was of course a mixture of air and hydrocarbon; it was not affected by fuming oil of vitriol, nor was bromine-water discoloured by it. It was hence inferred that no perceptible quantities of the olefiant series were present, and the temperature of collection is sufficient guarantee for the absence of any known members of the benzole series.

The gas was treated over mercury, with solid potash and pyrogallate of potash successively, when it yielded—

1·27 per cent. of carbonic acid, and
6·58 „ „ oxygen.

The residue, analysed eudiometrically, gave the following results:—

Gas collected from the surface of Pennsylvanian Petroleum at a temperature of − 1° *C., freed from Carbonic Acid by Potash and from Oxygen by Pyrogallic Acid.*

	Observed Volume.	Pressure m.	Temp. Cent.	Corrected vol. at 0° C. and 1 m. pressure.
Gas	133·1	0·3099	9°·	39·934
Do. + air	392·8	0·5666	9·	215 47
Do. + do. + oxygen	465·6	0 6391	8·2	288 92
After explosion	421·3	0·5940	10·	245 09
After absorption of CO_2	383·4	0·5515	8·	205·23
After addition of hydrogen ..	474 3	0 6395	3·8	299 15
After explosion	346·5	0·5062	4·	172·86

Deducting the nitrogen, or 23·4 vols. = 54 per cent. of the original gas, we have here a relation of hydrocarbon to condensation and carbonic acid, as—

16·534 : 43·83 : 39·86
or, 100 : 265 : 241.

The oxygen consumed amounts to 67·16 vols., or 4·06 times the volume of the hydrocarbon. The members of the olefiant and benzole series being absent, it may fairly be inferred that the hydrocarbon resembles in constitution the liquids with which it is associated; and if this be the case, the gas must be a mixture of the hydrides of ethyl and propyl, the former of which requires a relation of hydrocarbon to condensation and carbonic acid, as—

$$1 : 2{\cdot}5 : 2$$

while the hydride of propyl requires a relation of 1 : 3 : 3. By calculation from the numbers above, it can be shown that the gas analysed must have consisted of a mixture of these gases in nearly equal proportions, or of—

C_2H_6, hydride of ethyl 7·94
C_3H_8, hydride of propyl 8·01

—the correctness of which is confirmed by the amount of oxygen consumed being about the mean of the quantities required for the combustion of these hydrides separately.

Hydride of ethyl requires 3·5 times its volume of oxygen.

Hydride of propyl requires 5 times its volume of oxygen.

The gas floating over the surface of the petroleum is therefore composed of—

Carbonic acid	.. ..	1·27
Oxygen ..	. ..	6·58
Nitrogen	.. ..	54·
Hydrocarbon	$\left\{\begin{matrix}C_2H_6\\C_3H_8\end{matrix}\right\}$	38·15

In this condition the gas is not explosive, and would only become so on being mixed with a large volume of air.

The most volatile liquid obtained by collecting the very first runnings from the stills employed in the process of refining petroleum has a specific gravity of 0·666. It is not sensibly affected by nitric acid, by oil of vitriol, or by bromine. When distilled, it begins to give off bubbles of gas in abundance at about 25° C., but after a few minutes all appearance of boiling ceases, although large quantities of gas and condensable liquid continue to pass over up to 65° or 70° C., and the whole liquid is evaporated below 100° cent.

This liquid resembles very closely the "kerosolene" or "kerosoform" which an American physician of New York has introduced as an anæsthetic agent; and I am indebted to Dr. Simpson for the opportunity of comparing it with a specimen of the latter. The specimen lent me by Dr. Simpson was quite indifferent to the above reagents. It had a specific gravity of ·6336. It began to boil at 28° C., and was almost completely volatilised at 70° C., so that it must have been composed almost exclusively of a mixture of the hydrides of amyl and hexyl, while the crude volatile product from the manufactory contained, in addition to these hydrides, some incondensable gaseous products, and a considerable quantity of the hydride of heptyl.

The incondensable gases dissolved in this most volatile liquid were expelled by gently warming a large quantity (about two gallons) of liquid, and passing the gases, before collecting them over water, through a long metallic worm, surrounded by a freezing mixture composed of ice and salt, the whole apparatus having been filled previously with carbonic acid to expel air.

The first two portions which were collected showed, after separating carbonic acid and oxygen, little difference in composition from that already analysed, and which had been collected from the surface of the crude oil.

I omit the details of the analyses of these two, and submit only the results, which correspond in both cases with a mixture of the hydrides of ethyl and propyl.

	Gas.		Condensation.		Carbonic Acid.
I.	8·289	:	22·947	:	19·045
	100	:	2·77	:	242
	Oxygen consumed .. 32·338				
II.	7·275	:	20·70	:	17·586
	100	:	280	:	240
	Oxygen consumed .. 31·07				

The gas coming over a little later from the same liquid was found to approach nearer in composition to pure hydride of propyl, as is shown by the following analysis. This portion was treated with potash before being introduced into the eudiometer, but the oxygen which it contained was not separated before combustion, but was estimated in a separate experiment, and found to amount to 2·44 per cent. of the gas burned.

	Observed Volume.	Pressure.	Temperature.	Corrected vol. at 0° and 1 m. pressure.
Gas	39·723	0·2817	15·1	10·604
After addition of oxygen.. ..	160·	0·3939	16·	59·548
After addition of air	260·128	0·4917	14·5	121·46
After explosion	236 386	0·4680	16·5	104·33
After absorption	204·386	0·451	15·	87·276
After admission of hydrogen ..	357·161	0·602	14·	204·53
After explosion	231·225	0·4613	13·6	102·29

Deducting the nitrogen and the 2·44 per cent. of oxygen contained in the gas, we have here the ratio of hydrocarbon to condensation and carbonic, acid, as

5·984 : 17·13 : 16·954
·100 : 286 : 283

Hydride of propyl C_3H_8 = 2 vols., requires a ratio of 1 : 3 : 3.

The quantity of oxygen consumed by the hydrocarbon is 4·67 times its volume, while pure hydride of propyl would require 5 times its volume.

The gas collected at a still later period from the same liquid was free from carbonic acid, oxygen, and nitrogen gases, and agreed in composition with a mixture of the hydrides of propyl and butyl.

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° and 1 m. pressure.
Gas	43·034	0·2821	19·5	11·335
After addition of oxygen.. ..	151·465	0·3857	19·9	54·454
After addition of air .. .	417·	0·6439	20·6	249·70
After explosion	372 644	0·6038	16·7	212·05
After absorption	321·	0·566	15·2	172·11
After addition of hydrogen ..	405·	0·649	17·	247·45
After explosion	353·032	0·5846	15·2	195 52

The relation here of hydrocarbon to condensation and carbonic acid is as—

11·335 : 37·65 : 39·94
100 : 332 : 352

The oxygen consumed is 5·88 times the volume of gas burned,

while hydride of butyl alone requires 6·5 times its volume of oxygen for combustion.

The gas evolved on warming the light spirit of petroleum, as it is prepared for sale, after having been kept, however, for some months in a vessel not hermetically sealed, was found to be a mixture of nitrogen and oxygen, with nearly pure hydride of butyl.

After separating by potash the carbonic acid which had been allowed to occupy the space above the liquid, the gas was analysed; the oxygen which it contained was estimated by pyrogallate of potash in a separate experiment, and amounted to 15·37 per cent.

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° and 1 m. pressure.
Gas	73·2	0·2399	7·	17·25
After addition of air	273·3	0·4360	5·2	117·11
After addition of oxygen.. ..	334·	0·4976	5·7	162·82
After explosion	288·5	0·4523	6·4	127·5
After absorption	228·5	0·3995	10·2	87·998
After admission of hydrogen ..	330·	0·5022	13·	158·2
After explosion	317·	0·4799	12·2	145·86

Deducting the nitrogen and oxygen contained in the gas, we have here a relation of hydrocarbon to condensation and carbonic acid as,—

9·64 : 35·32 : 39·532, or as
100 : 366 : 409

closely corresponding to the relations in hydride of butyl, which are,—1 : 3·5 : 4.

The gas was therefore composed of—

28·74 nitrogen
15·37 oxygen
55·89 hydride of butyl

and it would appear from this experiment that the light volatile liquids absorb and retain oxygen in greater proportion than that element is contained in atmospheric air.

The liquid condensed by the freezing mixture during the collection of these gases, and that obtained by subsequently heating the large body of liquid from which they were expelled to a higher temperature, not exceeding however 30° C., or the boiling point

of hydride of amyl, was redistilled. It began to boil at 0° C.; a considerable portion passing over between 0° and 4° was collected separately; another fraction between 6° and 8° was also collected apart; the remainder nearly all distilled below 15° cent.

The liquid distilling between 0° and 4° C. is nearly pure hydride of butyl, which has not yet been described. It is a perfectly clear, colourless, very mobile liquid, having an agreeable sweet smell, but eluding, by its great volatility, the sense of taste. It is insoluble in water, but dissolves in alcohol and ether, and alcohol of 98 per cent. absorbs between 11 and 12 times its volume of the vapour at a temperature of 21°·5 C. It burns with a yellow, not very luminous flame. Mixed in the gaseous state with twice its volume of chlorine, liquid chloride of butyl is formed, and the original 3 volumes become condensed into 2 volumes of hydrochloric acid.

The specific gravity of the liquid at 0° C. is 0·600. It is therefore the lightest liquid at present known.

The vapour-density determined by Dumas' method, the vapour being absorbed by alcohol, gave the following results:—

Temperature of air	13·8 C.	Temperature of sealing	40° C.
Barometer	·7615 m.	Capacity of globe	185·6 cc.
Empty globe	30·577 grms.	Air bubble	7·8 cc.
Globe and substance	30·788 grms.	Temperature of alcohol	14° C.

Hence vapour-density = 2·11.

Hydride of butyl, C_4H_{10}, requires by calculation 2·006.

The liquid, analysed eudiometrically in the gaseous state, gave the following numbers:—

Analysis of Butyl Hydride.

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° and 1 m. pressure.
Gas	35·04	0·1944 M.	5° C	6·691
After addition of oxygen.. ..	326·	0·4810	4·8° C	154·11
After explosion	294·8	0·4507	4° C	130·95
After absorption of CO_2	256. 9	0·4215	9° C	104·33

Hence we have,—

Gas.		Condensation.		Carbonic Acid.
6·691	:	23·16	:	26·12
100	:	346	:	390

or,

Hydride of butyl requires—

100 : 350 : 400

The liquid collected between 6° and 8° C. is not very different from this last. It is, however, a mixture of hydride of amyl with hydride of butyl. Its sp. gr. at 0° C. was found to be ·6004. The vapour-density was 2·178, and the composition in the gaseous state is shown by the following numbers:—

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° and 1 m. pressure.
Gas	15·3	0·4392	19·3	9·39
After oxygen	264·5	0·6912	19·3	185·22
After explosion	223·	0·6509	17·9	149·12
After absorption	166·8	0·6154	19·5	106·78

Hence we have,—

Gas.		Condensation.		Carbonic Acid.
9·39	:	36·10	:	42·34
100	:	384	:	450

or,

Hydride of butyl requires,—

100 : 350 : 400

It was not to be expected, from the manner in which the gases were collected, that any single portion would correspond exactly in composition with any member of the series, and some attempts which were made to separate the gases from each other by washing with alcohol, did not yield more conclusive results than those already obtained with the mixtures.

From the foregoing experiments we may, I think, safely conclude, that all the homologues of marsh gas, excepting marsh gas itself, are present in the liquid as it comes to this country, and there appears to be little doubt that marsh gas, and perhaps even free hydrogen, will be found among the gases which are evolved with the oil at the springs.

XII.—*On the Action of Chlorine upon Arsenious Acid.*

By Charles L. Bloxam.

Being desirous of preparing a considerable quantity of terchloride of arsenic by a more direct method than those usually prescribed, for which arsenic itself must first be obtained, I distilled a mixture of arsenious acid with strongly ignited charcoal-powder in a current of washed and dried chlorine. This process furnished very much less than the calculated quantity of terchloride of arsenic, and the residue in the retort was found to contain a large quantity of arsenic acid, notwithstanding that a considerable excess of charcoal had been employed. This led me to examine the action of chlorine upon arsenious acid itself.

When powdered arsenious acid is very gently heated in a current of chlorine, the gas is absorbed, a colourless liquid distils over, and the powder melts to a perfectly transparent and colourless liquid, which solidifies to a transparent glass on cooling. On continuing the action of heat and chlorine upon the fused mass, it gradually volatilises entirely, with evolution of oxygen.

Liquid product of the action of chlorine upon Arsenious acid.—This liquid had all the characters of terchloride of arsenic.

8·28 grains of it, when decomposed by water and precipitated by nitrate of silver, gave
19·84 grns. of chloride of silver, corresponding to
4·9081 grns. of chlorine, or 59·27 per cent.

Pure terchloride of arsenic contains only 58·67 per cent.

On redistilling the liquid, almost all of it passed over between 267° and 268° F.*

9·69 grns. of the redistilled liquid, decomposed by water and precipitated by hydrosulphuric acid, gave 6·52 grns. of tersulphide of arsenic, representing 3·9756 grns. of arsenic, or 41·02 per cent.

9·79 grns. gave 23·29 grns. of chloride of silver, representing 5·7616 grns. of chlorine, or 58·85 per cent.

These numbers prove the liquid to be terchloride of arsenic, containing as might be expected, a trifling excess of chlorine:

* Gmelin states the boiling-point of terchloride of arsenic to be 132° C. (269·6° F.) apparently on the authority of Dumas.

	Eqt.	Calculated.	Found.
As	75·0	41·32	41·02
Cl_3	106·5	58·68	58·85
	181·5	100·00	99·87

The action of chlorine upon arsenious acid may be recommended as a convenient laboratory process for the preparation of terchloride of arsenic.* Since the solidification of the residue always cracks the retort, it is better to employ a Florence flask in which a tubulated aperture has been made with the help of the blowpipe, to receive the tube delivering the chlorine. With a moderately long-necked flask no condenser is necessary, and the terchloride may pass at once into the receiver. 1,000 grns. of dry powdered arsenious acid will be found a convenient charge, and will require the chlorine from about 20 measured ounces of common yellow hydrochloric acid and 1,500 grns. of black oxide of manganese. As a slow current of chlorine is required, the mixture must be very gently warmed, the chlorine being passed first through water and then through oil of vitriol.

Arsenious acid yields rather less than one-third of its weight of terchloride of arsenic.

Solid product of the action of chlorine upon arsenious acid.—The vitreous residue cracked in all directions, with some violence, in the act of cooling, splitting glass tubes and bulbs containing it, and often projecting fragments of them to some distance. Brilliantly transparent when freshly prepared, it gradually became opaque throughout when kept for a few days, like vitreous arsenious acid. When moistened with water it became opaque, and on boiling gradually dissolved, yielding a strongly acid solution which deposited crystals of arsenious acid on cooling. The solution was found to contain arsenic acid, arsenious acid, and a small quantity of hydrochloric acid.

10 grns. of the vitreous mass yielded only 0·23 grn. of chloride of silver, representing 0·05 grn. chlorine, or 0·5 per cent.†

The amount of arsenious acid was determined by dissolving the

* It is mentioned by Dr. Miller, in his "Elements of Chemistry," 1864; Part II. p. 689, my experiments upon it being then in an incomplete state.

† Wallace (Phil. Mag. Nov. 1858) obtained a glassy substance by the action of hydrochloric acid upon arsenious acid, to which he assigned the composition $2AsO_3$, $AsClO_2$, requiring 10·9 per cent. of chlorine.

glass in solution of potash, acidulating with hydrochloric acid, and adding a standard solution of permanganate of potash.

The result of this determination in several different specimens of the glass showed that the proportion of arsenious acid varied very considerably, as might be expected, from the difficulty of arresting the action of chlorine at a definite stage.

Some experiments were therefore made upon the direct synthesis of the glass with arsenious and arsenic acids.

At the closed end of a tube of hard glass some arsenious acid was placed, and in front of it a layer of arsenic acid in powder, the latter was heated to a temperature below its melting-point, and after some time the vapour of arsenious acid was driven over it by applying heat to the end of the tube, when the arsenic acid liquefied immediately, forming a glass similar to that obtained by the action of chlorine.

A mixture of one equivalent (99) of arsenious acid with one equivalent (115) of arsenic acid was found to undergo fusion at a far lower temperature than arsenic acid alone, but did not form a transparent glass. When two equivalents of arsenious acid were employed, the glass was quite transparent.

In the experiments recorded in the following table, the mixtures of arsenious and arsenic acids were heated in bulbs blown in the centre of tubes, open at both ends, until a perfectly clear liquid had been produced. The ends of the tubes, with any excess of arsenious acid which had sublimed, were then cut off, the bulb with its contents weighed, soaked in weak potash until the vitreous mass was dissolved off, and again weighed to ascertain the weight of the vitreous mass; the arsenious acid was then determined in the solution by acidifying with hydrochloric acid, and adding a standard solution of permanganate of potash:—

	AsO_3 in eqts. employed.	AsO_5 in eqts. employed	AsO_3 found in 100 parts. Of the mixture.	AsO_3 found in 100 parts. Of the glass.
I*	2	1	63·25	55·30
II	3	1	72·00	61·76
III	4	1	77·40	66·34
IV	5	1	81·10	63·02
V	5	1	81·10	66·63

* A little arsenious acid sublimed during the fusion. even in this instance.

These results render it probable that when arsenious acid in excess is fused with arsenic acid, the compound $2AsO_3.AsO_5$ (containing 63·25 per cent. of AsO_3) is formed, though it is difficult to obtain it in a perfectly pure form, because the temperature at which it is decomposed is but little above that at which the last portion of the excess of arsenious acid volatilises.

After very careful fusion of arsenious acid in chlorine, arresting the action as soon as a perfectly clear liquid glass was produced, the latter was found to contain 62·38 per cent. of arsenious acid ($2AsO_3.AsO_5$ requires 63·25).

In several of the earlier experiments it had been observed that the period at which fumes of terchloride of arsenic ceased to be evolved at a moderate heat, and at which the liquid glass had just become transparent, was that at which the glass weighed 88 to 89 per cent. of the arsenious acid employed.

According to the equation—

$$11\ AsO_3 + Cl_6 = 2\ AsCl_3 + 3\ (2AsO_3.AsO_5)$$

100 grns. of arsenious acid should furnish 86·2 grns. of the vitreous residue, containing 63·25 per cent. of arsenious acid, whilst the terchloride of arsenic produced should amount to one-third of the weight of the arsenious acid, as was, in fact, the general result of the experiments.

For the equation—

$$8\ AsO_3 + Cl_6 = 3\ (AsO_3.AsO_5) + 2\ AsCl_3$$

100 grns. of arsenious acid should yield 81 grns. of the glass, containing 46.26 per cent. of arsenious acid, whilst the terchloride of arsenic produced would amount to nearly half the weight of the arsenious acid (45 per cent.)

The conclusion to which I have been led by the foregoing experiments is, that the action of chlorine upon arsenious acid at a moderate heat consists in the oxidation of one portion of arsenious acid at the expense of another, the arsenic of which is converted into terchloride, whilst the arsenic acid which has been formed combines with the remainder of the arsenious acid to form a transparent glass, having the composition $2AsO_3.AsO_5$, which may also be produced by heating arsenic acid with an excess of arsenious acid.

XIII.—*On a Crystallised Hydrate of Phenylic Alcohol.*

By F. Crace Calvert. F.R.S., F.C.S.

I observed some time since that when four parts of carbolic acid were well agitated with one part of water, and the whole exposed to a temperature of 4° C., the sides of the containing vessel became lined with fine large crystals, which proved, on more careful examination, to be six-sided prisms of the rhombic system. This new substance was found to be soluble in water, alcohol, and ether, and to melt at a temperature of 16° C. To ascertain its composition some of the crystals were taken and carefully dried between folds of blotting paper, and then submitted to analysis, when the following results were obtained:—

0·435 of substance gave 0·260 of water, or 6·67 of hydrogen, and 1·112 of carbonic acid, or 69·65 of carbon.

In a second analysis, 0·488 of substance gave 0·301 of water, or 6·85 hydrogen, and 1·243 of carbonic acid, or 69·5 of carbon.

These results correspond in composition to a bihydrate of phenyl, or to the ordinary hydrate of phenyl + 1 eq. water, as seen by the following formulæ:—

	$C_{12}H_5O.HO$	$C_{12}H_5O.2HO$	$C_{12}H_5O.3HO$.	Found.
Carbon.....	76·59	69·90	64·29	69·13
Hydrogen	6·38	6·80	7·14	6·72
Oxygen	17·03	23·30	28·57	24·15
	100·00	100·00	100·00	100·00

The above figures show that the substance analysed is ordinary phenylic alcohol, which has taken an equivalent of water to form a new crystalline compound, and what further substantiates this opinion is that when it has been liquified by a temperature above 16° C., and heat is applied, it gradually loses water, and the boiling point of the liquid rises until it reaches 187° C., the boiling point of phenylic alcohol.

This is, I believe, the first instance of an alcohol uniting with one equivalent of water to form a crystallized hydrate. The only apparent exception with which I am acquainted is the hydrate of propyl-alcohol discovered by Erlenmeyer. I say apparent,

because, from the short extracts I have been able to read of his paper, it does not appear that he has separated the water which forms the hydrate of the alcohol obtained by him; in fact, the product appears to distil without decomposition.

The neutrality of bihydrate of phenyl on litmus paper, as well as that of the ordinary hydrate, led me to enquire if the ordinary hydrate should be considered an acid, as stated in most of our text-books (as carbolic or phenic acid), or as an alcohol, or as a body having some similar properties to glycerin.

To decide this point I made the following series of experiments: I took 100 cub. cent. of solutions of caustic potash, having the following specific gravities—1·02, 1·03, 1·04, 1·06, and added successively to each of them 25 cub. cent. of the ordinary hydrate of phenyl, perfectly pure, and having a melting point of 34° C.

The following table gives the results observed:—

Specific gravity of caustic potash.	25 c. c.						
1·02	On adding 25 c. c. of the ordinary hydrate of phenyl to 100 c. c. of solution caustic potash of the above strength, the mixture separated into two layers—the upper layer consisting of 104 c. c., a solution of carbolic acid in alkali, and the lower layer of 21. c. c. carbolic acid, which has taken up a certain amount of water.						
1·03	25 c. c. No suspension.	25 c. c. No suspension.	25 c. c. No suspension.	On adding, as before, hydrate of phenyl to solution of caustic potash of the above strength, it was not until the addition of the 3rd measure of 25 c. c. that the mixture separated into two layers; the upper layer = 45 c. c., and the lower one = 130 c. c.			
1·04	25 c. c. No suspension.	25 c. c. No suspension.	25 c. c. No suspension.	25 c. c. No suspension.	In this instance it required 100 c. c. carbolic acid before separation took place, when the following results were obtained:—Higher layer = 13 c. c. of alkaline solution, and lower layer = 187 c. c. of acid solution.		
1·06	25 c. c.	25 c. c.	25 c. c.	25 c. c.	25 c. c.	25 c. c.	25 c. c. In this instance, even after the addition of 175 c. c. of carbolic acid, no separation took place.

The above experiments clearly show that the solubility of phenic acid in the alkaline solution is not due to a combination of the acid with the alkali, for in that case the quantity of phenylic acid which would have entered into solution would have increased in ratio to the quantity of potash in solution, whilst no such ratio exists, and therefore no combination.

What further substantiates this view is, that if to 100 c. c. of alkaline solution of sp. gr. 1·03 is added successively 25 c. c. of carbolic acid, the first two enter into solution, but on a further addition of 25 cub. cent, not only do they remain undissolved, but they separate or carry down with them nearly their own bulk of acid, which had been previously held in solution. This novel fact of the separation of a substance already held in solution by the simple addition of a further quantity of the same compound, proves beyond all doubt that an alkaline solution acts only as a solvent for the hydrate of phenyl, and is therefore not a combination of carbolic acid with oxide of potassium.

The above table also illustrates another interesting fact, viz., that if to a solution of alkali of sp. gr. 1·06 is added successively 25 c. c. of pure carbolic acid, no separation takes place; for we were able to add 200 c. c. of hydrate of phenyl without any of it separating. This is due, probably, to the fact that the hydrate of phenyl takes up a certain amount of water, which reduces its specific gravity until it is almost identical with that of the alkaline solution.

Further. Two volumes of liquified hydrate of phenyl were mixed with one volume of concentrated caustic ley, and the mixture distilled in a retort, when 98 % of the original acid passed over into the receiver, whilst the 2 % left in the retort was decomposed into a resinous matter, due to the oxidizing action of the alkali upon the carbolic acid.

I may state that these experiments were repeated with the bihydrate of phenyl, when precisely similar results were obtained, if the quantity of water it contains is taken into account, leaving no doubt that they are identical bodies, with the exception that the new hydrate contains 1 eq. more water, not of composition, but simply of crystallization.

It is stated in our text-books that phenic acid is prepared by mixing the oils of tar, which distil between 150° C. and 200° C., with a highly concentrated solution of caustic potash, and that the whole, on cooling, forms a white crystalline mass. If we repeat

this process, substituting for the oil of tar pure hydrate of phenyl, a white solid mass is also obtained, which, on being pressed a great number of times between folds of blotting paper, so as to remove as near as possible the whole of the excess of alkali, a white crystalline mass is obtained, which proves, on examination, to be crystals of hydrate of phenyl contaminated with a little alkali.

Carbolic acid absorbs with great avidity dry ammoniacal gas, but no combination takes place, for if the mixture is heated the ammonia gas is expelled, not a trace remaining in combination with the acid.

It is barely necessary to add that if the ammoniacal carbolic acid is heated in a closed tube, water and aniline are produced.

Both the hydrates of phenyl, when heated with oxide of lead, dissolve it, and both form a solid compound. These, on being well washed with water to remove all excess of phenic acid, and dried, are found on analysis to have an identical composition, viz., $C_{12}H_6O_2 + 2PbO$.

This compound is slightly soluble in hot alcohol, and deposits on cooling.

As a solution of both the hydrates of phenyl give, with a solution of subacetate of lead, a white bulky precipitate (which contracts on drying in a remarkable manner, remaining as a white amorphous powder), I made the following series of experiments to ascertain if the precipitates which are produced under these circumstances have a constant composition. For this purpose I mixed 200 c. c. of a saturated solution of the ordinary hydrate with 10 c. c. of a solution of subacetate of lead, containing 1·614 of oxide of lead. The precipitate produced was collected, washed slightly, and dried at 110° C., when 1·090 grm. of it gave, on calcination, 0·698 grm. of oxide of lead, or 64 % PbO.

In another experiment I took the same quantity of carbolic acid solution, and added to it double the quantity of subacetate of lead. In this instance the quantity of oxide of lead in 100 parts of the precipitate was equal to 68·2 %, showing that in this precipitate there was 4 % more oxide of lead than in the preceding one, and therefore that there is no definite compound formed; in fact, there is so little affinity between hydrate of phenyl and oxide of lead that if one of the above precipitates is washed several times with boiling water, it loses a large proportion of the hydrate of phenyl. In one instance, for example, 0·470 grm. of the above

washed precipitate (dried again, of course, at 110 C.) gave, on calcination, 0·393 grm. of oxide of lead; consequently, the precipitate contained 83·6 % of oxide. There can, therefore, be no doubt that the hydrate of phenyl, like many other organic substances, does not give any well-defined compound with oxide of lead.

Lastly. Carbolic acid does not decompose alkaline carbonates even under the influence of heat. The small amount of carbonate which disappears is not decomposed, but merely enters into solution.

From the above facts I conclude that what has been called carbolic or phenic acid is a neutral compound, and must be regarded as the hydrate of an alcohol, and the new substance described by me is the bihydrate of the same radical.

XIV.—*On the Action of Silicate and Carbonate of Soda on Cotton Fibre.*

By F. Crace Calvert, F.R.S., F.C.S.

I have lately been engaged in investigating a case of injury to goods, which I hope will prove interesting to chemists and manufacturers, from the novelty of the ascertained chemical facts to which the injury is traceable.

A large quantity of blue-dipped indigo cotton goods, with white reserves, were shipped two or three years ago to South Africa, and when opened some time after their arrival, were found so unsound as to be quite unsaleable, the cotton fibres being so much injured as to give way upon the slightest strain. The goods were, therefore, returned to this country, and placed in my hands to investigate the cause which had produced this damage.

As a large number of bales were returned without having been opened abroad, an excellent opportunity offered itself for selecting a well-defined series of pieces for experiments, and also for judging of the effects of packing on goods generally, when exposed for a long period to the hot and moist atmosphere of tropical climates.

Firstly, on opening the bales, I observed that the boiled-oil cloth which had been employed to protect the goods from external damp, yielded, when subjected to a very slight strain, proving that the texture of the cotton fibre had been injured by the oxidation it had undergone, in consequence of its having been saturated with boiled oil.

Secondly, on examining the goods forming the bales, it was found, in every instance, that the outer folds, including the second, and sometimes the third, were stained and dirty, but this did not extend deeper, the inner folds being perfectly free from stain or mildew. These facts show the importance of returning to this country (where claims are intended to be made upon the manufacturers or packers) entire and unopened bales of goods, instead of a few sample pieces, which cannot show the state of the bales, and enable the examiner to speak with certainty as to the cause of injury.

I also ascertained that the rottenness of the fabrics could not have been caused by their having been packed in a damp condition, for the hygrometric moisture of a piece in the centre of a bale did not exceed 8·5 per cent. Further, the goods were carefully examined to ascertain if any mildew could be discovered, which would have occurred if the goods had been packed in a damp state, and which would certainly have developed itself more fully in the interior of the bales than nearer the outside, if damp packing had been the cause. What completely removed from my mind all doubt as to the cause, was that, on carefully examining the pieces composing the bales, I found among the injured pieces, some which were quite sound, and on submitting these pieces to analysis, comparatively with those which were injured, the following results were obtained:

The sound pieces left only from 0·55 to 0·65 of ash, whilst the injured pieces left 8·29 and 8·59 of ash, the composition of which was as follows:—

	No. 1.	No. 2.
Insoluble Silica	2·94	3·81
Silica combined with soda	2·35	2·53
Soda	1·77	1·60
Other salts, Sulphate of soda, Chloride of sodium, Sulphate of lead, &c.	1·23	0·65
	8·29	8·59

These analyses show that the pieces had been finished with silicate of soda, which had undergone a partial decomposition; while the pieces which left only a few thousandths of ash were found, on further examination, to have been finished in the ordinary way, viz., with amylaceous substances. This induced me to examine

more minutely the goods, to ascertain whether it was to the silicate of soda, or to the carbonate of soda, arising out of its decomposition, that the injury sustained was due; and I was further prompted to carry on this investigation from the fact that at the present time the tendency amongst manufacturers is to weight their goods. It is well known that the risk of mildew is considerably increased in proportion to the weight of size; consequently there is a great inducement to use mineral in preference to vegetable substances for that purpose. I, therefore, trust that the results now published will warn manufacturers of the risk they run in using mineral size, without great care and experience, whilst on this point I may be permitted to give here an insight into the nature of the size often used in Lancashire for sizing the warps of grey calicoes, and, therefore, I give a few of the results obtained at my laboratory.

Analyses of Various Cloths.

No. 1.

Mineral matter, principally clay and sulphate of magnesia	5·2
Water in excess	2·8
Fermented flour	10·0
Hygrometric moisture	8·0
Fibre	74·0
	100·0

No. 2.

Mineral matter, principally sulphates of baryta and magnesia	4·5
Water in excess	2·1
Fermented Flour	11·3
Hygrometric moisture	8·0
Fibre	74·1
	100·0

No. 3.

Mineral matter, principally sulphate of soda and clay	4·8
Flour	10·0
Water in excess	4·5
Hygrometric moisture	8·0
Fibre	72·7
	100·0

No. 4.

Mineral matter	1·24
Water in excess	1·74
Fermented flour	13·02
Hygrometric moisture	8·00
Fibre..	76·00
	100·00

The above data show that warps are sized with sour flour (viz., flour which has been allowed to ferment for several days or weeks) and various mineral matters, to the amount, irrespective of moisture, of about 15 per cent. There can be no doubt that goods thus sized are extremely liable to mildew, owing on the one hand, to the use of fermented flour or organic matter in a state of decay, and on the other, to the use of clay, which tenaciously retains moisture, which facilitates cryptogamic vegetation when the goods are packed. I may state, *en passant*, that sulphate of magnesia, sulphate of lime, sulphate of baryta, sulphate of soda, and the chlorides of sodium and magnesium are often used, with or without clay, as weighting materials.

On examining the comparative strength of various pieces composing a bale, I observed that the outside folds of the pieces which formed the external parts of the bale (above alluded to as dirty and stained) were comparatively strong when tested against the folds of the same piece which were towards the interior of the bale. I therefore took the same weight of cloth from both classes of folds and submitted them to analysis, with the following results:—

	Interior of bale.	Exterior of bale.
Insoluble silica	4·81	7·08
Silica combined with soda ..	2·53	0·20
Soda	1·60	0·47
Other salts	0·65	0·55
	8·59	8·30

On examining and comparing these figures, it is at once seen that the stained fold shows a large increase in the amount of insoluble silica, and a corresponding decrease in the amount of silica combined with soda; but, notwithstanding this, the total amount of silica is nearly the same in both classes of cloths.

Further, that there is a total disappearance in the stained fold, of 1·13 %, or more than two-thirds, of the total amount of soda. From these results it would appear that the silicate of soda, when first applied to the goods, contained the whole of its silica in combination with the soda, and that under the influence of the carbonic acid of the atmosphere, the silicate of soda has been decomposed into insoluble silica and carbonate of soda, thereby giving rise to great increase in bulk; whilst in the goods which were protected from an excess of moisture—as towards the interior of the bales,—and also from the action of carbonic acid, there is only a partial decomposition of the silicate of soda. Mr. Walter Crum has kindly suggested, and I believe the view to be correct, that the cotton fibre has, by its organic nature, a cohesive attraction for silica, which enhances the decomposition of the silicate of soda employed to finish and weight the goods.

From these facts we may assume that there were two destructive influences brought to bear upon the cotton-fibre—1st, that of the increase of bulk resulting from the decomposition of the silicate of soda, giving rise to the formation of free silica and carbonate of soda, which exercised a distending and disintegrating action upon the cellular tissue of the cotton fibre, causing it to burst, and necessarily weakening its tensile strength; 2nd, the direct and destructive action of the free carbonate of soda upon the fibre. The latter appears to be the principal cause of injury, for in the external folds we have a more complete decomposition of the silicate, as shown in the above figures, by the increase in the amount of insoluble silica, and at the same time a decrease of the soda, amounting, as previously stated, to more than two-thirds of the total weight.

We shall now trace more in detail this interesting decomposition of silicate of soda, and endeavour to show what had become of the soda which had disappeared. To attain this object a complete series of specimens were obtained from an entire bale, viz.: 1, a piece which formed the outside and was stained; 2, some of the paper employed in wrapping the goods, which was in immediate contact with the stained cloth; and, 3, some of the flax wrapping placed next to the paper and between the latter and the oil-cloth covering above alluded to. The following are the results yielded by analysis:—

	Pieces of Goods.		Paper Wrapping.		Flax Wrapping.	
	No. 1. inside fold.	No. 2. outside fold.	No. 3. in contact.	No. 4. not in contact.	No. 5. in contact.	No. 6. not in contact.
Insoluble silica..	4·05	5·65	0·02	0·03	0·04	0·01
Silica combined with soda....	2·21	0·38	0·09	0·02	0·08	0·03
Soda.....	1·76	0·25	0·85	0·01	0·29	0·02
Other substances	1·96	1·91	15·15	15·28	1·19	1·25
Total ash	9·98	8·19	16·11	15·34	1·58	1·31

In examining these results we have again a most striking and marked difference in the amount of insoluble silica and soluble silicate of soda in the two different parts of the same cloth; and, further, where the carbonate of soda has been removed, the folds of the cloth remain comparatively sound. As to the paper wrapping, it is evident that the paper in contact with the goods has absorbed a great part of the soda which was previously combined with the silica, and that the soda is partly in the state of carbonate, and partly in combination with some of the organic matter of the brown paper; for when some of the paper was treated with water, it yielded a yellowish brown substance, which coloured the liquid, whilst the part of the same paper which had not been in contact with the goods did not discolour water in any marked degree. Further, the aqueous solution was neutral, and not alkaline, as in the previous case. As to the flax wrapping, the same difference as noted in the paper was observed, viz., that the part of the wrapping in contact with the stained paper and the stained fabric contained carbonate of soda, whilst that which was in contact with the clean paper contained only a trace. In looking over the bales, a piece of cloth was found, which had been finished with silicate of soda, and was partly overlapped by another piece, showing one half of its exterior fold stained and comparatively sound, whilst that half of the fold which was prevented from forming the exterior of the bale by being overlapped by the previous one was quite tender and rotten, though it showed no signs of any stains or mildew. I also examined a sound piece which had lain in contact with an injured one, and found that in those folds which had been in contact, there was in the injured piece less soluble silicate, and in the folds of the sound piece a considerable quantity of carbonate of soda, the presence of which could not be found in the folds forming the centre of it.

Having observed that the reserved white patterns of the blue-dipped Indigo cloth were a great deal more tender than the blue portions of the same piece, I carefully cut out a portion of the white parts and submitted them, with the blue parts, to analysis, with the following results :—

	White.	Blue.
Insoluble silica	5·48	3·17
Silica combined with soda	0·18	2·10
Soda	0·78	1·43
Other salts	1·08	0·67
Total	7·52	7·37

These figures illustrate the fact that the decomposition of the silicate of soda has been carried on to a much greater extent in the white parts than in the blue; and I am led to believe that the cause of the increased rottenness in the white is due to the printer having used a resist-paste too acid, and having found that the whites were slightly tendered, he endeavoured to check the further action of the acid on the cotton-fibre (which, as chemists well know, continues until the cotton fibre is completely destroyed) by the employment of a strong solution of silicate of soda, which, being an alkaline salt, was well adapted to neutralise any acid in the cloth and arrest its action. And as previously only weak solutions of silicate of soda had been employed for this purpose, the printer of these goods could not have foreseen that the use of a more concentrated solution would result in such serious consequences. The above figures also prove another interesting fact, viz., that the white parts of the cloth contain a much larger proportion of silicate of soda than the blues, thus proving that the dyed indigo fibres, being partially filled with this resinous dyeing material, were not in a condition to absorb so largely the silicate of soda.

Messrs. H. Caro & Dancer, who were also employed to investigate this matter, entertain a different opinion as to the cause of the white parts being more injured than the blues. These gentlemen are led to believe from their results that the reason why the whites are more injured than the blues is, that a slow chemical action has ensued between the sulphate of lead remaining from the reserve paste and the silicate of soda, and that a silicate of lead has been formed, and as this salt occupies a larger bulk than the sulphate of lead previously existing in the fibre, the production of it inside the cellular tissue of the fibre has been the cause of the increased

tenderness of the whites. But as these gentlemen are engaged in investigating the question more fully, I shall leave to them the pleasure of publishing their results.

Lastly, I deemed it my duty to make some direct experiments on the action of silicate of soda on cotton fibre. I therefore took some white cotton and dyed a portion of it with indigo. This blue-dyed cloth, with a part of the white one, were dipped in a moderately strong solution of silicate of soda, then dried, and a portion of them introduced into a bottle, at the bottom of which a little water had been placed, and to help the action of the carbonic acid of the *atmosphere*, a slow current of carbonic acid was then passed through the bottles containing the cloths. After three months time the warps of these samples were tested, and their comparative breaking weights were found to be as follows:—

	On an average of 10 essays.
The warps of the unsilicated cloth dyed blue	334
The same silicated	299 284 289

These results leave no doubt that the warps, even during the short period of three months, had been considerably injured by contact with silicate of soda. In conclusion, I beg to add that I am aware that silicate of soda has been used for finishing coloured goods, but when employed it has been in a very dilute state, and therefore its destructive action has not been sufficiently marked to draw the attention of calico printers.

XV.—*On some Hydrated Cupric Oxychlorides from Cornwall.*

By A. H. Church, M.A., Professor of Chemistry, R.A. College, Cirencester.

I have lately received from Cornwall a copper mineral which proves to be new. Qualitative analysis of the specimen shewed it to contain chlorine, copper, and the elements of water; very precise testings subsequently revealed the presence of traces of carbonic acid, arsenic, aluminium, and sodium; but these substances exist in most minute proportion in a carefully selected sample—indeed, their quantity is too insignificant to admit of estimation.

The colour of the new mineral is bright blue, slightly inclining to green (turquoise-blue); it occurs in thin crusts, consisting of irregular aggregations of minute globules, which present a botryoïdal appearance under the microscope. The globules are distinctly subcrystalline and subtranslucent. The hardness of the mineral approaches 3; its density has not been determined with exactness, but it is about 3·5. The streak of the new mineral is white; it is extremely fragile. It is insoluble in water, but quite easily soluble, without residue, even in dilute acids and in ammonia. It is hygroscopic: when kept in dry air, it loses some hygroscopic water without change of colour, but it rapidly becomes green at 100°, acquiring a tint similar to that of atacamite: this change of colour is accompanied by a further and considerable loss of water. On ignition, the cupric chloride volatilizes in part; the final residue is of a dark olive-green tint.

For analysis the mineral was dried *in vacuo* over oil of vitriol until it ceased to lose weight; the sample had been most carefully selected, in order that the results of the analysis might be completely free from the disturbing influence due to any impurities; for under the microscope it was seen that the botryoïdal or pisolitic crusts, although constituting the bulk of the mineral, were accompanied by traces of foreign salts. These salts were calcic sulphate,* ferric oxide, &c.; the latter oxide being also the matrix of the mineral. The following are the analytical details:—

I.—1·185 grammes lost *in vacuo*	·055 gramme water.	
II.—1·13 grammes gave	·505 gramme chloride of silver.	
III.— ·598 gramme gave	·281 gramme chloride of silver.	
IV.—1·13 grammes gave	·748 gramme cupric oxide.	
V.— ·752 gramme gave	·499 gramme cupric oxide.	
VI.— ·405 gramme gave	·268 gramme cupric oxide.	

A third determination of chlorine was made in another sample which was less pure, containing compounds of calcium and iron in more than mere traces. Not having the requisite data for correcting the result, I have omitted it, relying upon the numbers above given, the accuracy of which I have no reason to doubt. The greater part of the single specimen of the new mineral was

* A complete analysis of Connellite, a cupric sulphato-chloride (from Cornwall), is greatly to be desired. In the outer blue layer, or crust of our mineral itself, a trace of sulphuric acid was found: but 212 milligrammes gave 2 milligrammes only of barium-sulphate.

consumed in these analyses, for some of which I took, as will be noticed, an unusually large amount of substance in order to lessen the effect of any errors of manipulation.*

Translated into percentages the experimental results are as follow:—

I.	Hygroscopic water lost *in vacuo* ..	4.64 p.c.	
II.	Chlorine	11·05 p.c.	in the mineral after drying *in vacuo*.
III.	Chlorine	11·62 p.c.	
IV.	Cupric oxide	66·19 p.c.	
V.	Cupric oxide	66·39 p.c.	
VI.	Cupric oxide	66·17 p.c.	

To what formula do these percentages correspond? There is but one native hydrated cupric oxychloride—atacamite, but it contains more chlorine than the salt now under review. Atacamite seems often to have the composition expressed by the formula:—

$$CuCl_2.3CuH_2O_2.aq.;$$

sometimes it has a smaller percentage of water, sometimes it is more highly hydrated. The formula which furnishes proportions most nearly approaching to the blue oxychloride is—

$$CuCl_2.4CuH_2O_2.4aq.,$$

as the following comparison of the theoretical and experimental percentages will shew:—

		Theory. $CuCl_2.4CuH_2O_2.4aq.$		Experiment. mean.
2Cl	71·0	.. 11·91	or 11·91	11·33
Cu....	63·5	.. 10·64	} 66·60CuO	66·24
4CuO ..	318·0	.. 53·29	}	
$8H_2O$ ..	144·0	.. 24·16	24·16	——
	596·5	100·00	102·67	

The new mineral thus differs chemically from the allied species atacamite in a most unmistakeable manner. Not only is it more highly hydrated, but it contains the cupric chloride and cupric hydrate in different proportions.

* A special determination of impurities, zinc-oxide, &c., was made in one instance; they amounted to ·75 per cent. on the vacuum-dried mineral.

	$CuCl_2$	:	CuH_2O_2
Atacamite	1	:	3
New species	1	:	4

The physical characters of the two minerals are also, as I have already remarked, very distinct. A few words as to the water in the mineral may not be out of place here. Crystallized cupric chloride is green, and has the formula $CuCl_2.2aq$. When this salt is dissolved in some quantity of water, it becomes blue; just so the less hydrated mineral atacamite is green; the more hydrated new species is blue. So also with the blue langite and pale blue lyellite, as compared with the green brochantite.

Atacamite....	$CuCl_2$.	$3CuH_2O_2$.	aq. *green.*
New species..	$CuCl_2$.	$4CuH_2O_2$.	4 aq. *blue.*
Brochantite ..	$2CuSO_4$.	$5CuH_2O_2$	*green.*
Langite*	$CuSO_4$.	$3CuH_2O_2$.	aq. *blue.*
Lyellite.....	$\left.\begin{matrix}CuSO_4\\CuSO_4\end{matrix}\right\}$.	$3Cu_2H_2O_2$.	3 aq. *blue.*

The following details concerning the atacamite recently detected in Cornwall are given in part for the sake of comparison.

These are the results on analysing an extremely pure specimen:—

I. 11·24 grains lost ·27 grains *in vacuo.*
II. 11·98 grains lost 2·05 grains at 270°C.
III. 11·24 grains gave 6·07 grains AgCl.
IV. 12·8 grains gave 7·1 grains AgCl.
V. 11·24 grains gave 7·85 grains CuO.
VI. 11·38 grains gave 7·89 grains CuO.

The formula $CuCl_2 . CuH_2O_2 . aq.$, demands the following percentages:—

2Cl	71·0	15·97 or	15·97	
Cu	63·5	14·26	71·43	CuO
3CuO . ..	238·5	53·58		
$4H_2O$	72·0	16·19	16·19	
	445·0	100·00	103·59	

These are the percentages deduced from the foregoing analyses of atacamite:—

* Or, for the sake of more ready comparison with brochantite, langite may be represented thus: $2CuSO_4.6CuH_2O_2.2aq.$

Hygroscopic water lost *in vacuo* ..	I.	2·40 p.c.
H_2O lost at 260°C.	II.	17·11 p.c.
Cl	III.	13·35 p.c.
Cl	IV.	13·70 p.c.
CuO	V.	69·84 p.c.
CuO	VI.	69·34 p.c.

Analysis II. does not represent the percentage of water in atacamite accurately. It was observed that this mineral does not lose water alone when heated in the oil-bath to 260° C. Hydrochloric acid is also evolved, while a part of the water is yet obstinately retained, even at the temperature at which cupric chloride begins to be given off. The numbers deduced from Analyses III. to VI. require a correction to be made in them for hygroscopic water (see Anal. I.) before they can be compared with the theoretical percentages:—

	Experiment. (Mean corrected p.c.)	Theory. ($CuCl_2.3CuH_2O_2.aq.$)
Cl ..	.. 15·20	15·97
CuO ..	.. 71·31	71·43
H_2O ..	.. ——	16·19
		103·59*

The deficiency in the experimental and calculated chlorine and cupric oxide is most probably due to the hygroscopic water not having been absolutely removed by desiccation in vacuo over oil of vitriol; its influence has consequently been under estimated. The proposed formula agrees more nearly with the results of analysis than the expressions usually adopted for the several varieties of atacamite:—

$CuCl_2.3CuH_2O_2$
$CuCl_2.3CuH_2O_2.1\frac{1}{2}aq.$
$CuCl_2.3CuH_2O_2.2aq.$
$CuCl_2.3CuH_2O_2.3aq.$

In all these formulæ, however, the proportion of cupric chloride to hydrate is maintained constant. It is worthy of note, that not only have several varieties of atacamite been prepared artificially, but that a compound corresponding to the salt described in the

* The whole of the copper is calculated as oxide, part being in fact combined with chlorine.

first part of the present communication has been obtained by Kane and by Graham, by the action of water on the compound $CuH_3N_2Cl_2$:—

Kane's Salt..	$CuCl_2.4CuH_2O_2.2aq.$
New Cornish mineral ..	$CuCl_2.4CuH_2O_2.4aq.$

The atacamite from Cornwall (St. Just) occurs in a variety of forms. The mineral is sometimes found as hollow stalactitic tubes, the concentric layers of which are almost transparent. Sometimes it appears in semicrystalline crusts, more or less distinctly stratified, and having a rippled surface. The proximity of the copper mine in which the mineral is found, to the sea, and the detection of sodium and magnesium salts in the atacamite itself, point to the mode of its formation.

I am indebted to the kindness of Mr. R. Talling, of Lostwithiel, for all the minerals mentioned in the present note.

Notes to the foregoing paper.—Some indications of the existence of another cupric oxychloride, more basic than the new species described, have been observed. Until additional specimens have been met with, it would, however, be premature to make any positive statements on this point.

The new oxychloride is not affected by boiling with water. No cupric chloride enters into solution, nor is the colour of the mineral altered. An intimate union seems to exist between the cupric chloride and hydrate in the new mineral. Its formula (omitting the 4 aq.) might perhaps be written on a mixed HCl and H_2O type ($2HCl + 8H_2O$) :

$$H_{18}\begin{Bmatrix}Cl_2\\O_8\end{Bmatrix} \qquad Cu''_5H_8\begin{Bmatrix}Cl_2\\O_8\end{Bmatrix}$$

I have mentioned that the new oxychloride contains a trace of some sodium-salt. It seems to be the chloride, and is removed by washing the mineral with hot water. The quantity is trifling. 511 milligrammes of the finely powdered mineral gave by this treatment but 3 milligrammes of silver chloride. I deemed it a matter of some interest to determine the chlorine in the mineral thus washed. Accordingly, a portion was dried over oil of vitriol *in vacuo* till it ceased to lose weight. Of this preparation ·353 grammes gave ·17 grammes silver chloride. This quantity

corresponds to 11·91 per cent. of chlorine, exactly the proportion demanded by the formula I have adopted.

All the insoluble basic cupric minerals already alluded to, if finely powdered, dissolve easily in dilute acids. On this property might be founded a method of volumetric analysis, the ratio of chloride (or sulphate) to hydrate being, I believe, thus ascertainable.

Postscript, March 11th, 1865. The new oxychloride occurs in the Botallack mine. Thanks are due to the captain of this mine, Mr. Hockin, for his obliging courtesy. Mr. Talling has now found and forwarded to me a further supply of the new blue oxychloride. Some of the specimens are on quartz. One of the new specimens gave the following results on analysis (substance dried *in vacuo*):

·264 grm. gave ·175 grm. CuO = 66·29 p. c.
·3555 grm. gave ·235 grm. CuO = 66·10 p. c.

Theory demands 66·60 per cent. The chemical and physical characters of this species are therefore constant as well as distinct.

XVI.—*On some Hydrated Cupric Oxysulphates from Cornwall.*

By A. H. Church.

Lyellite.—Not very long after his announcement of "Langite" as a new mineral species from Cornwall, Prof. Maskelyne pointed out a second copper compound, from the same locality, as distinct. This species he termed "Lyellite." Three months later, M. Pisani gave an analysis of the same mineral; it will be found in the *Comptes Rendus*, of Nov. 14th, 1864. M. Pisani re-names the mineral "Devilline," and deduces for it the formula:—

$$(\dot{C}u\dot{C}a\dot{F}e)_3\ddot{\ddot{S}} + 3aq.$$

I purpose to employ the name *Lyellite*, as having priority.

I have received from Mr. Talling a portion of the same specimen of lyellite as that analysed by M. Pisani, and have submitted it to analysis. It is unnecessary to repeat in detail the physical and chemical characters of this new species of Prof. Maskelyne's; it will suffice to say here that the analysis of this mineral presents

some peculiar difficulties. For, intermixed with the true lyellite, which occurs in concretionary crusts of a very pale bluish white tint, and satiny lustre, is a darker blue mineral, apparently langite. This impurity occurs in layers, and is irregularly distributed in the whiter mineral; these layers are sometimes in the direction of the radiation, sometimes across it. Fortunately the blue mineral, being in loosely coherent masses of minute crystals, may be almost completely removed by breaking the mineral into small fragments, and carefully brushing these with a fine sable pencil. In this way my specimen was prepared for analysis, but it was not *quite* pure even then. I believe the only impurity was the blue mineral, and assuming this, as is most probable, to be langite, the discrepancies between the theoretical and experimental percentages are explained. Lyellite contains copper, calcium, a sulphate, and the elements of water. It contains also a minute trace of iron, so minute as to give no distinct reaction when a few grains of the mineral in solution were tested with potassic ferricyanide; and even after oxidation, the ferro-cyanide gave a faint blue coloration only.

The following are the results of the analysis of lyellite:—

·3245	gramme	lost *in vacuo*	·002	gramme	H_2O
·3225	„	gave	·184	„	$BaSO_4$
·3225	„	„	·045	„	$CaCO_3$
·3225	„	„	·165	„	CuO

These numbers correspond to the following percentages:—

Hygroscopic water	·62	per cent.
SO_3	23·50	„
CaO.	7·81	„
CuO.	51·13	„

I have said that M. Pisani proposes for this mineral the formula—

$$(\dot{C}u\dot{C}a\dot{F}e)_3\dddot{S} + 3aq.$$

We have, however, seen that it contains no iron, and the results of my analysis, which agree closely with those obtained by M. Pisani, correspond to a slightly modified formula. Annexed are the theoretical and experimental percentages.

	Theory. ($CuCa2SO_4$. $3CuH_2O_2$. 3aq.)		Experiment. Pisani.	Church.	
$4CuO$	318	49·53	51·01	51·13	
CaO	56	8·72	7·90	7·81	
$2SO_3$	160	24·90	23·65	23·50	
$6H_2O$	108	16·95	16·60	16·88	(by diff.)
	642	100·00	99·16	0·68	(impurities).
			FeO 2·77	100·00	
			101·93		

It will be observed that the cupric oxide is in excess, while the calcium-oxide and sulphuric anhydride are deficient; the assumed admixture of the lyellite with a mineral evidently (from its deeper blue tint) richer in copper, will account for all these discrepancies—a very small percentage of langite would in fact produce this result.

Brochantite.—A mineral which appears to have the chemical characters of brochantite has been lately found in Cornwall. M. Pisani announced this discovery in the *Comptes Rendus* for Nov. 28th, 1864. Several formulæ have been proposed for the native and the artificial brochantites, but it has been remarked that this basic sulphate oscillated between—

$$CuSO_4.2CuH_2O_2 \text{ and}$$
$$CuSO_4.3CuH_2O_2;$$

my analysis points in the same direction; it suggests, however, the intermediate formula—

$$2CuSO_4.5CuH_2O_2.$$

Before giving the analytical results, it may be stated that the brochantite often accompanies langite, the latter mineral being then seen as a scattered blue crust upon the dark green or emerald-green brochantite. I fear that the crystals in my specimens are too small and confused for accurate measurement. They are transparent, and occur in groups of slender wedges, tapering towards either extremity. Two of the boundaries of each crystal appear curved. Since my preliminary note on Cornish brochantite appeared in the *Chemical News* (Feb. 10th, 1865), this mineral has been described, under the name of Waringtonite, by Professor Maskelyne; it is unnecessary, therefore, to repeat here the physical characters of the substance; I will merely give the analytical results and the formula they

suggest. It ought to be stated that the utmost care was taken to obtain a homogeneous sample for analysis.

The brochantite occurs upon decomposing elvan, but immediately underneath the cupric crust, a considerable quantity of ferric oxide occurs. An impure cupreous wad also occasionally accompanies the brochantite.

6·73 grains lost		·07	grains at 260° C.	
5·17	„ gave	·03	„	insoluble residue
5·17	„ „	2·85	„	$BaSO_4$
6·73	„ „	4·62	„	CuO
5·17	„ „	3·51	„	CuO.

Before the mineral was submitted to analysis, it was placed over oil of vitriol *in vacuo;* but by this treatment it suffered no appreciable loss. Below are given the percentage numbers deduced from the foregoing analyses. In the first column the percentages are those deduced directly; in the second column the calculations have been made, after subtraction of the water lost at a temperature not exceeding 260° C.,* and of the insoluble matter :—

CuO	68·27	69·32
SO_3	18·93	19·24
H_2O	11·18	11·44
H_2O lost below 260°	1·04	
Insoluble matter	·58	100·00
	100·00	

The formula $2CuSO_4.5CuH_2O_2$, requires percentages closely corresponding with those deduced from the analyses :—

	Theory.	Experiment.
CuO	69·00	69·32
SO_3	19·84	19·24
H_2O	11·16	11·44

The differences, it will be observed, all lie in the direction of the probable experimental errors. In an analysis not recorded above, 6·73 grains of the mineral gave 3·39 grains of $BaSO_4$; this corresponds to 17·3 per cent. of SO_3. But with the lower estimate of the SO_3, the *total* percentage of water in the mineral, calculated by difference, amounts to no more than 13·48; in the second analysis it is only 12·6. These numbers exclude the formula $CuSO_4.3CuH_2O_2.aq.$, which demands 15·34 p.c. H_2O, as the following comparisons show. It must be remembered that the

* Some specimens lose nothing at this temperature.

mineral under review loses sulphuric acid as well as water when heated sufficiently to deprive it of all water; the water in it is retained even at 260°—270° C.

	Theory.			Experiment.		
	I. $CuSO_4$ $3CuH_2O_2$.	II. $CuSO_4$ $3CuH_2O_2aq$.	III. $2CuSO_4$ $5CuH_2O_2$.	I. Pisani.	II. Maskelyne.	III Church.
CuO ..	70·36	67·62	69·00	70·06	68·24	69·32
SO_3 ..	17·70	17·04	19·84	17·52	16·73	19·24
H_2O ..	11·94	15·34	11·16	13·42	14·64	11·44

Collating the recent with the older analyses of Brochantite,* there seems some ground for the opinion that at least two substances, chemically distinct, have been included under one name. If such be the case, Prof. Maskelyne's Waringtonite might be separated chemically as well as crystallographically from Brochantite, although his proposed formula (II. above) is negatived by both of my analyses, and as well as by those of M. Pisani. One hesitates, indeed, between the formulæ I. and III., but it is possible that M. Pisani may not have analysed the true wedge-shaped crystals of so-called Waringtonite, but the commoner form of Brochantite occurring in the same locality.

For the analysis of the variety or species Waringtonite, I am indebted to my assistant, Mr. R. Warington, junior.

Langite.—According to M. Pisani, langite has the formula $CuSO_4.3CuH_2O_2$. aq., the very expression assigned to Waringtonite by Prof. Maskelyne. My own results confirm those of M. Pisani. A few words are necessary as to the material submitted to analysis.

Langite appears both in minute prismatic crystals of a fine blue colour, and also as a foliated crystalline mass. The latter form is the more abundant, and having freed some specimens of it from a few imbedded crystals of the deeper colour, I submitted them to analysis, with the following results:—

a. Air dried.	1·024	gramme	lost *in vacuo*	·004	gramme	H_2O
	1·024	„	gave	·691	„	CuO
	1·024	„	„	·501	„	$BaSO_4$
b. Vacuum dried.	14.09	grains	lost at 100° C	·12	grains	H_2O
	14·09	„	below redness	2·29	„	H_2O
	14·09	„	gave	6·86	„	$BaSO_4$

* Rammelsberg's *Mineralchemie* (1860), p. 268.

c. Dried at 100° C.	12·3 grains gave	8·35 grains CuO

I made the analyses of *a*; *b* and *c* were analysed by Mr. Warington. The following are the percentages deduced from the several analyses, calculating the results on the vacuum-dried substance, and also on the substance as dried at 100°C.:—

	Dried *in vacuo*.		Dried at 100°C.
	A. H. C.	R. W.	R. W.
CuO ..	67·48	67·31	67·88
SO_3 ..	16·79	16·72	16·88
H_2O ..	15·73	16·25	15·53
	100·00	100·28	100·29

These numbers correspond very closely with those required by the formula $CuSO_4.3CuH_2O$. aq.:—

			Mean (vacuum dried).
4CuO ..	318 =	67·65	67·40
SO_3 ..	80 =	17·02	16·76
$4H_2O$ ..	72 =	15·33	15·89
	470	100·00	100·05

The results of independent analyses by M. Pisani, Mr. Warington, and myself, are so exactly accordant, that there cannot be the slightest doubt that the blue foliæ said to be langite are definite in composition, and that the formula expressing the composition of the mineral is $CuSO_4.3CuH_2O_2$.aq. All the slight differences between the theoretical and experimental percentages lie in the direction of the several probable errors; and the loss of water *in vacuo* amounting to no more than ·39 per cent., it cannot be said that the mineral has been altered by the method of desiccation adopted. The total amount of impurities in the mineral was found by experiment to be very insignificant, yet, if allowance had been made for it, a still closer coincidence between theory and experiment would have been shown.

It is scarcely necessary to add that all the analyses recorded in the present paper were performed with the greatest care; the reagents were pure, and the methods known to be trustworthy.

XVII.—*On Vapour-densities.*

By J. Alfred Wanklyn.

In having recourse to a vapour-density determination for the purpose of settling a chemical formula, chemists are in the habit of preferring determinations made at a high temperature to those made at a low temperature. And yet they do not adhere to this principle with steadiness; for no one would think of preferring a vapour-density determination of alcohol above the boiling point of mercury to one at the boiling point of water. Chemical compounds are decomposed at high temperatures, and organic compounds especially. When the vapour-density at a low temperature differs from that at a high temperature, what is to show that the difference is not an effect of decomposition, and that the data obtained at high temperatures are of more value than those of a vapour-density determination of alcohol taken at temperatures above the boiling point of mercury?

Looking at the matter from this point of view, one would be inclined to reverse the maxim which has found favour with chemists, and to direct that a vapour-density determination, if it is to be employed for the construction of a formula, should be taken at the lowest temperature that is practicable. The reason which has induced chemists to run the risk of decomposing their vapours before measuring them (a risk which is very real) is the fear that vapours are not sufficiently gaseous at low temperatures. On the present occasion I will examine the grounds of this fear.

The results flowing from the accumulated labours of chemists in this direction may be summed up as follows:—

(1). Of a thousand vapours which have been experimented upon, all exhibit a density often almost identical with, and seldom departing from the theoretical density by more than about ·1 or ·2 when the determination is made at not less than 40° C. above the boiling point of the corresponding liquid. When the determination is made within about 10° C. of the boiling point of the liquid, the vapour-density determination is ·1 or ·2 higher than that at 40° C. above the boiling point.

(2). Some few substances, such as sulphur and acetic acid, have

vapour-densities, which taken at 40° C. above their boiling points, depart from the theoretical numbers by units instead of by tenths. On heating the vapours of some of these substances still higher, they become of the theoretical value in some instances,—in other instances not.

(3). Some substances, a vapour-density determination of which has been sought at 40° C. above the boiling point, give irregular numbers, and are known to decompose.

Respecting this last class of substances nothing need be said. Concerning Class (1) the remark may be made that the circumstance that, when no decomposition occurs, a determination made by the usual methods at 40° C. above the boiling point is better than one at only 10° C. above the boiling point, does not prove that accurate determinations cannot be made at within 10° C. of the boiling point if certain precautions be adopted.

On a former occasion I have pointed out that there is nothing magical in this elevation of 40° C., but that 40° C. *of super-heating* of the vapour—a condition which can be attained otherwise than by actual elevation of the temperature to 40° C. above the boiling point of the liquid—is the essential condition for vapour-density purposes.

This conclusion, which is a very natural and obvious deduction, almost evident *a priori*, has been tested by direct experiment. Dr. Playfair and the author selected a number of substances at random, converted them into vapour, superheated the vapour, not by raising the temperature, but by depressing the pressure (or what comes to very nearly the same thing, by mixing it with a certain volume of a permanent gas), and got accurate determinations of vapour-density at temperatures even below the boiling point.

Cahours' maxim, "heat your vapour 40° C. above the boiling point of the liquid," when emended into "superheat your vapour 40°," is quite compatible with the recommendation to "make the determination at the lowest temperature that is practicable."

Touching the slight increase in the vapour-density, when instead of 40° C. of superheating, there are only 5° C. or 10° C., it is not so much due to any alteration in the co-efficient of expansion, as to condensation on the walls of the vessel which is used to contain the vapour.*

Of Class (2) (the most prominent members of which, sulphur

* Certain experiments made by Magnus show that the effect due to this cause must be very considerable.

and acetic acid, evolve vapours irregular in their density at low temperatures, but regular at high temperatures), the observation may be made that there are good grounds for believing decomposition to occur in each individual case.

One needs but to glance at the poly-sulphides, to be convinced that sulphur is very prone to combine with itself and so to produce complex sulphur of different molecular weights. The existence of the allotropic modifications of sulphur points undeniably in the same direction. If we did not know that when we volatilize sulphur, we get vapour which alters in vapour-density on being heated, we might very reasonably expect such to be the fact.

Respecting acetic acid, there are good reasons for supposing it to be a bibasic acid. It has a great tendency to form double salts with monatomic bases. It forms a compound with butyric acid, viz., Butyr-acetic acid, an acid of considerable stability, which, as is well known, was for some time mistaken for propionic acid. The existence of these double salts and of this double acid is best explained by assigning to acetic acid a double formula, viz:—

$$\begin{matrix} \overline{C}_2H_3 \\ \overline{C}_2H_3 \end{matrix} \overline{O}\overline{O} \begin{matrix} H\overline{O} \\ H\overline{O} \end{matrix}$$

which involves no *breach of atomicity, i.e.,* no assumption that the C, H, and O have other than their usual saturating capacity. Accordingly the vapour-density which acetic acid actually exhibits at low temperatures is in accordance with much of its chemical history.

Again, the state of condensation of chloride of acetyl and of acetic ether, points to the existence of such a compound as—

$$\overline{C}_2H_3\overline{O}.H\overline{O}$$

which we accordingly encounter in the vapours given off by acetic acid when we heat above 200° C.

From this it will be seen that the alteration in vapour-density observed when sulphur and acetic acid are heated, may, with considerable probability, be ascribed to decomposition.

The state of the argument is this: a vast number of substances of the most different chemical character and composition have had their vapour-densities taken, and have been found to evolve vapours, which so far as they have been examined, comport themselves like gases, if they be superheated 40° C. That vapours, no

matter what their chemical composition, behave like gases, appears thus as the result of a first-rate induction.

As a set-off to it we should need some example of irregularity in the vapour of a substance which is known to resist decomposition. How far the cases of sulphur and acetic acid fall short of this is sufficiently obvious.

XVIII.—*Note on a New Bromine-derivative of Camphor.*

By W. H. Perkin.

Having had occasion to make some experiments on Laurent's bromide of camphor $C_{10}H_{16}O.Br_2$, I found that when strongly heated on the sand-bath it was decomposed, with evolution of hydrobromic acid and formation of an oily body, which solidified after standing for several hours. As this fact is in direct opposition to the account of this substance as given by Gerhardt, who states that when bromide of camphor is distilled it is decomposed, yielding bromine and camphor, I thought it worth while to make a few experiments on the product of this reaction. I therefore prepared a quantity of this oily product, and for the purpose of removing hydrobromic acid, washed it with a hot dilute solution of potash; it was then separated from the alkaline solution by means of a pipette and transferred to a retort provided with a thermometer. On heat being applied, distillation commenced, with evolution of a little hydrobromic acid; the distillate was collected until the thermometer rose to about 60° C. above the boiling point of camphor. The receiver was then changed, and the portion which came over above that point collected separately. This on cooling became solid, but was evidently mixed with a small quantity of oily matter, which was removed by pressure between folds of bibulous paper, then dissolved in a small quantity of alcohol, and allowed to cool. In the course of a few hours, magnificent crystals separated, which on being recrystallized were perfectly pure. Analysis of a specimen burnt with chromate of lead gave the following numbers:—

I. ·4050 of substance gave
·7723 of carbonic acid and
·2412 of water.
II. ·3557 of substance gave
·6787 of carbonic acid and
·2140 of water.
III. ·4984 of substance gave
·4050 of bromide of silver.

The percentages calculated from these numbers agree closely with those required by the formula $C_{10}H_{15}BrO$, as the following comparisons will show:—

	Theory.		Experiment. I.	II.	III.
C_{10}	120	51·948	52·00	52·03	
H_{15}	15	6·493	6·61	6·68	
Br	80	34·632			34·57
O	16	6·927			
	231	100·000			

The change which bromide of camphor undergoes when heated may therefore be expressed by a very simple equation:—

$$\underset{\text{Bromide of camphor.}}{C_{10}H_{16}O.Br_2} = \underset{\text{Bromo-camphor.}}{C_{10}H_{15}BrO} + HBr$$

Bromo-camphor, when pure and slowly crystallized from alcohol, appears in transparent prisms very similar to sulphate of sodium, but smaller. When impure, it sometimes forms tufts of flattened prisms of considerable size.

The crystals of bromo-camphor are very brittle, and taste more like turpentine than camphor. Bromo-camphor has a slight odour of camphor. It is very soluble in alcohol and ether. It melts at from 76° to 77° C., and if agitated solidifies at 74° C., but sometimes, if left undisturbed, remains liquid until the temperature has fallen as low as 54° C. It boils at 274° C., with slight blackening and evolution of a little hydrobromic acid. It sublimes slowly even at the ordinary temperature.

A portion was heated to 180° C. in a sealed tube with alcoholic ammonia for 12 hours; slight decomposition took place, with for-

mation of bromide of ammonium, and a peculiar organic base; but the amount produced in this reaction is so small that I have not as yet attempted to investigate its nature.

Bromo-camphor, when mixed with bromine, liquefies apparently without evolution of heat, and if the bromine has not been added in too great an excess, gradually solidifies into a crystalline mass, somewhat similar to that produced by the combination of camphor with bromine. It is most probably a *bibromide of bromo-camphor*, $C_{10}H_{15}BrO.Br_2$, a view which has to some extent been corroborated by a quantitative experiment. The product, when heated, decomposes with evolution of hydrobromic acid, and on cooling solidifies into a crystalline mass, which probably contains a bibromo-camphor $C_{10}H_{14}Br_2O$.

XIX.—*On the Action of Hydrosulphate of Ammonia upon freshly precipitated Sulphide of Copper.*

By Charles L. Bloxam.

The circumstance that, in the ordinary course of qualitative analysis, hydrosulphate of ammonia is capable of dissolving sulphide of copper, is well known; but as I could not meet with any explanation of it, I have made some experiments which demonstrate the production of a soluble crystalline compound containing copper, sulphur, ammonia, and hydrogen, upon the formation of which the solubility of the sulphide appears to depend.

When freshly precipitated well-washed sulphide of copper (prepared from sulphate of copper and hydrosulphuric acid) was boiled for a minute or two, in a flask, with colourless freshly prepared hydrosulphate of ammonia (obtained by saturating solution of ammonia with hydrosulphuric acid, and adding an equal volume of the same ammonia), an appreciable quantity of the sulphide of copper was taken into solution.

To prove that this was not due to any sulphur accidentally mixed with the sulphide of copper, the portion left undissolved was rapidly washed, and again boiled with the colourless hydrosulphate of ammonia, when a fresh quantity was dissolved.

By boiling the sulphide of copper with hydrosulphate of am-

monia saturated with sulphur, a very large quantity could be dissolved, and the solution, when mixed with hydrochloric acid, deposited an orange coloured precipitate, very dangerously similar to that of sulphide of antimony.

When the solution of sulphide of copper in the strongly sulphuretted hydrosulphate of ammonia was allowed to stand for some hours in a well-closed bottle, it deposited very beautiful vermilion-red tufts of needles, resembling chromic acid, but of a brighter colour.

These crystals were partially decomposed by washing, the washings coming away very yellow, long after the adhering mother-liquor had been removed, and furnishing a dark green precipitate of sulphide of copper when boiled.

If the partially washed crystals were rapidly dried over oil of vitriol, they assumed a fine copper-red colour, and suffered very little decomposition; but, in the moist state, they decomposed rapidly, evolving an ammoniacal odour, and becoming black. They suffered the same change in the water-oven.

On heating the crystals (dried over oil of vitriol) in a tube, they evolved a trace of moisture, and abundance of hydrosulphate of ammonia (judging by the smell), leaving a black residue, which evolved much sulphur when further heated.

Gently heated with water, the bulk of the crystals dissolved, leaving a black residue. The yellow solution became dark green and turbid on standing, and gave a black precipitate with hydrochloric acid.

Hydrochloric acid did not act upon the crystals in the cold, but, when heated, much hydrosulphuric acid was evolved, and a black residue left. No separation of sulphur was perceptible.

Nitric acid was also without action upon the crystals until heat was applied, when violent oxidation took place, and much sulphur was separated.

The analysis of the compound was effected by boiling with nitric acid until the sulphur had separated in pure yellow globules, which were collected and weighed.

The filtrate and washings from the sulphur were precipitated by chloride of barium, and the dissolved sulphur calculated from the weight of the sulphate of baryta. The filtrate from this last was precipitated by sulphuric acid, and after removing the sulphate of baryta, the copper was precipitated by boiling with potash.

The ammonia was determined in a separate portion by boiling

with hydrochloric acid till the compound was completely decomposed, removing the small quantity of dissolved copper from the solution by hydrosulphuric acid, and evaporating the filtered liquid, the residue of hydrochlorate of ammonia being carefully dried and weighed.

From the evolution of hydrosulphuric acid under the action of hydrochloric acid, it was inferred that the ammonia was associated with an equivalent of hydrogen, and it was therefore calculated as NH_4.

One of the specimens analysed had been rapidly dried over oil of vitriol, and the other by repeated pressure between folds of blotting-paper.

The results of the analysis were :—

			Calculated ($Cu_2NH_4S_7$*)
Cu....	32·65	32·11	32·81
S....	58·07	59·07	57·88
NH_4....	9·07	8·82†	9·31
	99·79	100·00	100·00

The formula which most nearly corresponds with these numbers, with a divergence which is scarcely to be avoided in dealing with a compound of this nature, would be $Cu_2NH_4S_7$.

Speculating upon the constitution of the compound, the two simplest rational formulæ which present themselves are $2CuS_3 . NH_4S$ and $2CuS . NH_4S_5$.

The mode of producing the compound would, of course, favour the latter formula, but I am inclined to prefer the former, because (1) there is no sign of the separation of sulphur on treating with hydrochloric acid; (2) of the absence of action on the part of cold nitric acid (conc.); and (3) of the action of heat upon the crystals.

In works upon qualitative analysis, it is often recommended that sulphide of potassium be substituted for hydrosulphate of ammonia as a solvent for the sulphur-acids existing in the hydrosulphuric acid precipitate, when copper is at all likely to be present; but I have often found that copper which might have have been overlooked in the analysis of a large mass of the remaining basic sulphides (*e.g.*, of bismuth and lead) has been easily detected, in consequence of its having passed out in the

* Cu = 31·7 NH_4 = 18 S = 16. † By difference.

hydrosulphate of ammonia solution, where it does not interfere with the investigation for arsenic, antimony, and tin.

XX.—*Notes upon the General Routine of Qualitative Analysis for Metals.*

By Charles L. Bloxam.

Reduction of Binoxide of Tin (Stannic Oxide) by Fusion with Cyanide of Potassium.—When stannic oxide is fused with cyanide of potassium of commerce, the whole of the tin is frequently not obtained in the globule of metal, a portion of it being converted into a sulphide by the sulphate of potash present in the cyanide. If the proportion of sulphate of potash be small, the rest of the tin is converted into stannous sulphide (SnS), which separates as a black powder on treating the fused mass with water; but if there be much sulphate of potash present, a portion of the tin assumes the form of stannic sulphide (SnS_2), which is found in the aqueous solution of the fused mass, from which it may be precipitated by hydrochloric acid.

10 grs. SnO_2 were fused with 50 grs. commercial cyanide of potassium (containing a little sulphate). The liquid mass had a clear yellow colour. The globule of tin weighed 7·1 grs. (calculated 7·8 grs.). On treating the slag with hot water, a considerable quantity of black SnS separated. The solution gave a very slight yellow precipitate with hydrochloric acid.

10 grs. SnO_2 were fused with 50 grs. of the same cyanide and 5 grs. sulphate of potash. The liquid mass had a brown yellow colour. The globule of tin weighed 6·6 grs. only. The slag, when treated with hot water, gave no black deposit, but the solution furnished an abundant yellow precipitate of SnS_2 when mixed with hydrochloric acid.

Since, in the final confirmation of the presence of tin, it is usual to fuse the supposed binoxide with cyanide of potassium, it is important, when using the commercial salt, to examine not only for metallic tin, but for any black sulphide separating during the solution of the fused mass in water, and for any yellow sulphide which may exist in the aqueous solution.

In the absence of cyanide of potassium, the ferrocyanide answers the purpose for reducing the stannic oxide, an alloy of iron with tin being obtained, which dissolves in hydrochloric acid, and responds to the test with mercuric chloride.

Detection of Zinc in Qualitative Analysis.—The absence of well-marked characters in the zinc-precipitates, and the dingy appearance of the sulphide when obtained in the ordinary course of analysis, combine to render the detection of minute quantities of this metal uncomfortable and unsatisfactory. To resolve any doubt, the analyst generally resorts to the blow-pipe test with nitrate of cobalt, but when this is applied in the ordinary manner, upon charcoal, to the sulphide of zinc, which is usually the last form assumed by the metal at the close of the analysis, it often fails to give satisfactory results. I have found the following mode of operating far more decisive:—The supposed sulphide of zinc is dissolved off the filter in hot nitric acid (dilute), the solution mixed with a very small quantity of nitrate of cobalt (not even enough to impart a pink colour), then with carbonate of soda in slight excess. The solution is boiled for a minute or two, the precipitate collected on a filter, washed, and the filter incinerated on platinum foil. The green colour is very bright if an excess of cobalt be avoided, and is best seen after the gritty residue has been powdered under a glass rod.

$\frac{1}{10000}$th of zinc can be at once precipitated by yellow hydrosulphate of ammonia from an ammoniacal solution. This proportion is not immediately indicated by ferrocyanide of potassium, though the solution becomes quite opaque on standing.

With $\frac{1}{5000}$th of zinc, the precipitate by ferrocyanide of potassium was formed immediately.

Detection of Magnesium.—Every analyst has remarked the frequent occurrence of a slight flocculent precipitate by phosphate of soda, where the characteristic crystalline precipitate of the ammonio-magnesian phosphate is expected. I have proved that this precipitate consists of phosphate of alumina, which is not mentioned, I think, in treatises upon qualitative analysis, as being likely to occur in this place.

Mineral Constituents of Filter-paper—Having met with some unexpected results in the course of qualitative analyses to test methods of effecting the separation of metals, I made a careful analysis of a considerable quantity of the ash of ordinary white filter-paper, bearing the name of "J. McA. and Co." (mill num-

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ber, 37). The ash consisted chiefly of silica and alumina, but contained considerable quantities of the carbonates of lime and magnesia, and of ferric oxide. There were also present small quantities of the sulphates of lime, potash, and soda, and mere traces of phosphoric acid, oxide of cobalt, and oxide of lead. Inasmuch as a single sheet of paper contained appreciable quantities of these constituents, and such a quantity is often employed in the course of an analysis, where it is exposed to the solvent action of acids, it appears to be necessary, in exact analysis, that the composition of the filter-paper should be recorded, with respect to the quality, as is now generally done with respect to the quantity of the mineral constituents.

XXI.—*On the Periodides of some of the Organic Bases.*

By William A. Tilden, Demonstrator of Chemistry in the Laboratory of the Pharmaceutical Society.

At different times have been described a number of substances, which are formed by the action of iodine upon certain of the organic bases, and particularly upon the natural alkaloids, in which the greater part of the iodine, however, enters into no very intimate state of combination, nor does any portion of it occupy the position of a substitute for hydrogen, since by simple treatment with nitrate of silver, the whole appears to be removed, at least in the majority of instances. Moreover, a considerable proportion of the iodine is capable of giving the usual reaction with starch, and, indeed, of being expelled with the vapour of water when the solutions of these compounds are boiled.

Some of the bodies thus formed are possessed of curious optical properties, the most interesting of which is perhaps the iodo-sulphate of quinine accidentally discovered some years ago by Dr. Herapath. Similar compounds have been prepared from codeine, papaverine, berberine, &c.; the only example of a sulphate with which I am acquainted being Herapath's quinine-salt.

A few months ago, in the course of some experiments upon caffeine, a solution of a few grains in aqueous hydriodic acid had been placed in a test-tube and forgotten. On examining the

contents of the tube after the lapse of a considerable time, it was found to contain a quantity of crystals of peculiar and beautiful appearance. They consisted of long prisms having a very fine greenish-metallic appearance. After several experiments I found that by dissolving caffeine in weak alcohol acidulated strongly with hydriodic acid, and then setting aside the mixture for a few days, a mass of crystals was deposited similar to those produced in the first instance, their formation being hastened by exposing the solution to light.

These crystals were collected, but it was found impossible to wash them with water, since by such treatment they entirely lose their lustre. A small quantity of very weak spirit containing a drop or two of coloured hydriodic acid may be used with great caution for removing the adhering mother-liquor, and they must be dried in vacuo, or in a current of dry air, since they are incapable of bearing the temperature of the water-bath.

This compound is extremely soluble in rectified spirit, forming a brown solution, from which, by spontaneous evaporation, a small quantity crystallizes, apparently unchanged; the greater part however, particularly when evaporated by the aid of heat, is deposited in small black nodules, being probably the same compound as that mentioned below.

The most interesting peculiarity of this substance consists in its action upon light. Examined under the microscope, the crystals are found to present all the characters of the polarizing crystals of Herapath. Unfortunately the light transmitted is considerably coloured, and I have been unsuccessful in preparing plates of sufficient size or tenuity to render them of any service optically.

For the determination of the iodine, the most convenient plan consists in suspending the powdered substance in water, and decomposing by the aid of sulphide of hydrogen or sulphurous acid, and subsequent precipitation by nitrate of silver.

I.—·2655 gramme of substance gave ..... ·3100 AgI
II.—·4895 „ „ „ ..... ·5702 „
III.—·5755 „ „ „ ..... ·6705 „
IV.—Burnt with chromate of lead and a pretty long coil of copper, ·5840 gramme gave ..... H_2O ·1345
CO_2 ·3622.

	I.	II.	III.	IV.	Mean.
Iodine ..	62·90	62·94	62·91	——	62·91
Carbon..	„	„	„	16·90	16·90
Hydrogen	„	„	„	2·48	2·48

These crystals, mixed with pure iron filings and heated in an oil-bath to 130—140° C., lost a quantity of water equal to 2·5–3 p. c.; a proportion so low as to be sensitive to small changes, and since this compound alters in appearance, even by long exposure in a vacuum over sulphuric acid, it is difficult to obtain it in an absolutely definite state. The results of experiment, nevertheless, point undoubtedly to the formula :—

$$2(C_8H_{10}N_4O_2I_3).3H_2O.$$

	Experiment.	Theory.
Carbon	16·90	15·92
Hydrogen ..	2·48	1·82
Iodine	62·91	63·18

In seeking to prepare this compound with greater facility, an attempt was made to obtain it by the addition of alcoholic iodine to a solution of the base in weak sulphuric or hydriodic acid, but by that plan I failed to procure anything but a deposition of black granules, which appeared to be crystalline. This black substance gave, in one experiment 74·13 p. c., in another 75·08 p. c. of iodine. It may possibly consist of another compound similar to that already described, but containing nine atoms of iodine, the formula of which would require 74·51 p. c.

It appears, then, that the gradual liberation of iodine in the solution is a condition necessary to the successful production of the polarizing crystals.

Bodies of this kind have generally been denominated simply periodides or teriodides, and I am not aware of any attempts to ascertain, experimentally, the position occupied by the iodine. Dr. Anderson has suggested that a portion may exist in the form of hydriodic acid, and in assuming two atoms (or four, as the case may be) to perform functions different from the other I believe him to be correct.

By means of a standard solution of hyposulphite of sodium I have made direct determinations of the amount of "free,"

or, as it may be termed, "exterior" iodine in the caffeine compound.

	I.	II.	Mean.
Experiment gave.....	40·22	40·83	40·52 per cent.

The formula may then be written thus :—

$$2\{(C_8H_{10}N_4O_2HI)I_2\}.3H_2O,$$

this arrangement indicating that four atoms or 42·12 per cent. of iodine is recognisable by starch, &c.

In order to test further this view of the constitution of these bodies, I thought it would be interesting to prepare, if possible, the periodide of an ethylated base, which should resemble the well-known teriodide of tetrethyl-ammonium. Accordingly, a quantity of caffeine was submitted to the action of iodide of ethyl at a temperature of 130° C. for about four hours. At the end of that time, the solution contained hydriodic acid and a little free iodine, and on gentle evaporation deposited a quantity of brilliant brown scales, which were comparatively little soluble in ordinary alcohol. On adding to the mother-liquor of these crystals a solution of iodine, best in hydriodic acid, a copious precipitation of the same compound is produced; and by simple recrystallization from alcohol, from which solvent it is deposited in glittering scales, this periodide is rendered pure and fit for examination. It bears without change or loss of weight the temperature of a water-bath, and was submitted to analysis in the manner already described; it is, however, attacked but slowly by hydrosulphuric or sulphurous acid, probably on account of its insolubility in water.

I.—·3010 gramme substance gave ·3530 AgI
II.—·4650 „ „ „ ·5448 „
III.—·4320 „ „ „ ·5028 „
IV.—·2775 „ „ „ ·3225 „
V.—Burnt with a mixture of chromate of lead and oxide of copper ·3805 gramme gave H_2O ·0978
CO_2 ·2790
VI.—·4860 „ „ H_2O ·1193
CO_2 ·3590.

	I.	II.	III.	IV.	V.	VI.	Mean.
Iodine....	63·22	63·31	62·89	62·77	——	——	63·04
Carbon....	„	„	„	„	19·99	20·14	20 06
Hydrogen..	„	„	„	„	2·83	2·71	2·77

The hyposulphite of sodium solution indicated 42·03 per cent. of free iodine.

The mean of the above results corresponds very closely with the numbers required by the formula $(C_8H_{10}N_4O_2.C_2H_5I)I_2$, as may be seen by the comparison exhibited below :—

	Experiment.	Calculated.
Carbon	20·06	19·86
Hydrogen	2·77	2·48
Total Iodine ..	63·04	63·07
Free Iodine ..	42·03	42·05

By digesting caffeine with alcohol and excess of iodide of ethyl for many days, I failed to convert the whole of the base into the ethylated compound: and as the iodide of ethylo-caffeine is very soluble, I was unable to submit that substance itself to analysis. By treating a quantity of periodide, however, with sulphuretted hydrogen, I was enabled to convert the base into platinum-salt. The chloroplatinate was found to be even more soluble than that of caffeine itself.

·3240 gramme gave ·0740 metallic platinum, corresponding to 22·83 per cent., the formula $C_8H_{10}N_4O_2.C_2H_5.PtCl_3$ requiring 23·02 per cent.

Iodide of methyl appears to furnish a crystalline iodide and periodide of methyl-caffeine with greater facility. The iodide crystallises in large colourless crystals, which are very soluble in water, less so in alcohol, and still less in ether.

·9810 gramme gave ·6825 AgI,

corresponding to 37·59 per cent. of iodine.

The formula $C_8H_{10}N_4O_2.CH_3I$ requiring 37·79 per cent.

On dissolving it in water and adding tincture of iodine, an abundant precipitate of periodide is formed, which, when recrystallized from alcohol, resembles much the corresponding body containing ethyl.

·5630 gramme gave ·6690 AgI, corresponding to 64·20 per cent. of iodine. The formula $(C_8H_{10}N_4O_2CH_3I)I_2$ requires 64·57.

When caffeine is heated with iodide of ethyl for a few hours only, a portion of the base is left unacted upon; and after precipitation of the whole of the ethyl-caffeine by means of iodine, it

slowly separates in brilliant crystals, which differ from the first described compound only in containing less water of crystallization.

I.—·5965 gramme gave ..... ·7128 AgI
II.—Burnt with a mixture of oxide of copper and chromate of lead, ·4495 gramme gave H_2O ·1085
CO_2 ·2678
III.—·4725 gramme gave ..... ·5622 „
IV.—·2730 „ „ ..... ·3255 „
V.—·4680 „ „ ..... ·5565 „

	I.	II.	III.	IV.	V.	Mean.
Iodine	64·57	——	64·31	64·43	64·25	64·39
Carbon	„	16·24	„	„	„	16·24
Hydrogen....	„	2·68	„	„	„	2·68

The amount of free iodine indicated was as follows:—

I.	II.	Mean.
42·34	43·03	42·68

The mean of the numbers here given corresponds with those demanded by the formula,

$$(C_8H_{10}N_4O_2HI)I_2 + H_2O.$$

	Experiment.	Theory.
Carbon.....	16·24	16·16
Hydrogen.....	2·68	2·18
Total Iodine....	64·39	64·14
Free Iodine..	42·68	42·76

In all the combustions made, the carbon numbers are a trifle too high. This may be from the large proportion of iodine and nitrogen present, the copper-turnings perhaps being prevented from very perfectly performing their office.

Pelletier has described an iodo-strychnine, to which he has assigned the formula

$$4(C_{21}H_{22}N_2O_2)I_6*$$

* I should write this $2(C_{21}H_{22}N_2O_2HI)I$.

and which is prepared by triturating iodine and strychnine together, and removing the hydriodate formed by means of boiling water.

This body is deposited from its alcoholic solution in orange-coloured scales, and contains theoretically 36·13 per cent. of iodine. When a solution of strychnine in dilute alcohol acidulated with hydrochloric or hydriodic acid, is mixed with alcoholic iodine, a brown precipitate is formed, which, when dissolved in boiling alcohol, crystallizes on cooling in very brilliant reddish-brown prismatic crystals. When dried they are extremely brittle, and very soon become reduced to a mere crystalline powder.

This compound contains no sulphuric acid, and does not lose weight when heated to 140° C.

I.—Burnt with a mixture of oxide of copper and chromate of lead ·5550 gramme gave..... CO_2 ·7102
H_2O ·1720

II.—·7198 gramme gave ..... CO_2 ·9198
H_2O ·2265

III.—Ignited with pure lime, ·5285 gramme gave.... ·5165 AgI

	I.	II.	III.	Mean.
C.....	34·90	34·84	——	34·87
H.....	3·44	3·49	——	3·46
I.....	——	——	52·81	52·81

These numbers agree very closely with those required by the formula $(C_{21}H_{22}N_2O_2HI)I_2$.

	Experiment.	Theory.
C.....	34·87	35·14
H.....	3·46	3·34
I.....	52·81	53·13

Pelletier has also described a compound of brucine, which contains 48·9 p. c. iodine. By heating this alkaloid by the same process as the strychnine, I obtained a substance which appeared to be identical with that described by Pelletier.

Attempts were made to prepare compounds of the same kind from other organic bases, aniline among the number, but without definite results.

XXII.—*On Phosphide of Magnesium.*

By Thomas P. Blunt.

As this substance does not appear to have been previously described, some account of its preparation and properties may prove interesting. The most practicable method of preparing it seemed to consist in heating the metal to redness in an atmosphere of phosphorus vapour. For this purpose an apparatus of the following form was used:—

A tube of glass, of difficult fusibility, was selected; two boats of a similar material were constructed, of such size as readily to enter the tube; one of these was filled with filings of magnesium, the other with fragments of phosphorus; both were then introduced into the tube, which was afterwards attached, by means of a plug of caoutchouc, to an apparatus for the evolution of carbonic acid dried by passing through sulphuric acid. The whole was so arranged that the stream of gas might pass over the phosphorus towards the magnesium. When the air was judged to have been expelled from the apparatus, the boat containing the magnesium was heated to strong redness by means of a Bunsen's burner. A gentle heat was then applied to the phosphorus, until it began to volatilize. The vapour was carried by the stream of gas over the heated magnesium, and at the moment when it reached the ignited metal, the latter burst into vivid combustion. In the first experiment the apparatus was allowed to cool immediately, and the product removed. The results obtained with it were anomalous. On treating a portion with dilute hydrochloric acid, a copious evolution of phosphoretted hydrogen (not spontaneously inflammable) took place. When the action had ceased, however, a black flocculent substance remained, upon which the dilute acid produced no action in the cold, nor was it dissolved to any extent upon boiling the liquid. This substance, as it afterwards appeared, was the true phosphide.

The evolution of phosphoretted hydrogen, however, was the cause of some perplexity, until an examination of the original substance suggested the following explanation:—The latter appeared to consist of a black powder (the pure phosphide), mixed with unaltered magnesium. It seemed probable, therefore, that

the intimate contact between these two bodies would produce a galvanic arrangement, in which, upon the addition of an acid, hydrogen would tend to attach itself, not to the unchanged metal, but to the phosphide. It would then, by virtue of the powerful affinities derived from its nascent condition, appropriate the phosphorus of the latter, and thus be converted into phosphoretted hydrogen. The truth of the above explanation was subsequently tested by making an intimate mixture of the pure phosphide, upon which dilute acids had been proved to exert no solvent action with metallic magnesium. Upon adding dilute hydrochloric acid, a copious evolution of phosphoretted hydrogen took place, as was expected.

A second operation, conducted in the manner already described, proved that, in order to prepare the phosphide in a state of moderate purity, it was only necessary to ensure the expulsion of air from the apparatus before heating the metal, and to continue the application of heat for a short time after the first appearance of combustion, maintaining at the same time the supply of phosphorus vapour. A minute proportion of unchanged metal, however, generally remains. When thus formed, phosphide of magnesium appears as a slightly coherent black mass, readily separated into a flocculent powder strongly resembling lamp-black, both in its appearance and physical properties. Its stability is most remarkable. It has been preserved unchanged for some weeks in moderately dilute hydrochloric acid; it has been boiled for some time with a mixture of equal parts of strong sulphuric acid and water, without apparent solution; and it is only with considerable difficulty that it can be dissolved in boiling nitro-hydrochloric acid, in which it has been boiled for hours without completely disappearing. It may be heated to redness without change, if air be excluded; in the presence of a current of air, however, oxidation takes place, and magnesia is gradually formed.

In order to ascertain the composition of this substance, the method of synthesis was adopted, the apparatus used being a slight modification of that above described. The metal, in fine filings, was introduced into a tube of hard glass, between two plugs of asbetos, the tube and plugs having been previously weighed. A second weighing, after the introduction of the magnesium, gave the quantity of the latter to be acted upon. The tube was now attached to a carbonic acid apparatus, and a bulb containing phosphorus. The rest of the operation was then con-

ducted as before, care being taken to expel the excess of phosphorus vapour from the tube as far as possible by continuing the stream of carbonic acid after the completion of the reaction. The tube was now detached and weighed, the increase of weight showing, of course, the amount of phosphorus absorbed by the known weight of magnesium. In every case a small quantity of metal escaped the action of the phosphorus, as was evidenced by the evolution of a few bubbles of phosphoretted hydrogen upon the addition of hydrochloric acid. The last and most successful operation, in which the evolution of gas was very small, gave a composition for the substance, approximating closely to the formula Mg'_3P. The quantity of metal used was 2·40 grains. The phosphide formed weighed 4·40 grains, giving thus a percentage composition of—

Magnesium.....	54·54	theory requiring	53·74 Mg'_3
Phosphorus.....	45·46		46·26 P.

It seems likely that an investigation, conducted on similar principles to the above, might dispel the uncertainty which at present rests upon the composition of the phosphide of calcium.

XXIII.—*On the Specific Refractive Energy of Elements and their Compounds.*

By J. H. Gladstone, Ph.D., F.R.S.

In February, 1863, the Rev. T. Pelham Dale and I sent to the Royal Society an account of some researches on the Refraction, Dispersion, and Sensitiveness of Liquids, which appears in the Philosophical Transactions for that year, pp. 317-343. We followed this up in the autumn by reading a paper at the meeting of the British Association at Newcastle, an abstract of which is to be found both in the Report of the Association itself, and in Les Mondes. In these two communications we showed the high importance of considering what we term the "specific refractive energy," that is, the refractive index minus unity divided by the density, or, in mathematical language, $\frac{\mu - 1}{d}$. Contem-

poraneously with our researches, Landolt was examining the same subject, and in a paper published in the last December number of Poggendorff's Annalen, he shows his familiarity with our paper in the Philosophical Transactions, and his ignorance of the abstract in the British Association Report. He gives much additional proof of the specific refractive energy being a real physical property of bodies, and has advanced the subject considerably in his attempt to show the influence of the atomic constitution of fluid compounds of carbon, hydrogen, and oxygen on the propagation of light.

In the original words of Mr. Dale and myself, "Every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when mixed with other liquids." This proposition may be extended to gaseous and solid bodies, the changes of temperature including those which affect the aggregate condition of the body, and the idea of mixture being enlarged so as to include ordinary cases of solution. Yet this general statement must be taken with a certain reserve. The influence of dispersion and, perhaps, other things, make the expression $\frac{\mu - 1}{d}$ rather an approximation to the truth than the truth itself; and our knowledge of the extent to which chemical combination may modify the specific refractive energies of the elements is as yet very limited.

Temperature.—That the influence of heat on the refraction of bodies is due to its altering their density, and that the specific refractive energy is the same, or very nearly the same, at all temperatures, was shown in our communications to the Royal Society; but it has received confirmation from the careful observations of Landolt on propionic acid, ethylic and amylic alcohols, aldehyde, and hydride of benzoyl.

That this law holds good notwithstanding the passage from the liquid to the solid state is apparent from the observations on water and phosphorus, in previous papers by Mr. Dale and myself;* and we have more recently measured the refractive index of sulphur at the melting point, or rather at the point when crystals began to form in the sulphur previously melted in our prism. The indices of four different parts of the spectrum were as follows :—

* Phil. Trans., 1858, p. 890, and Phil. Mag., July, 1859.

Line A.	Line D.	Line E.	Most refrangible limit.
1·9024	1·9295	1·9527	2·0065

The density of sulphur at this temperature was found to be 1·8063, which gives ·51 as the specific refractive energy for the line D. The refractive index of native sulphur at the ordinary temperature is stated by different observers to be 1·958, 2·008, 2·04, and 2·115, of which the mean is 2·03. The density is said to be 2·04. The specific refractive index of solid sulphur may, therefore, be taken at ·50 for the brightest part of the visible spectrum, a result coincident with that of ·51 for the line D as seen through melted sulphur, at least within the limits of experimental error.

No experiments have been made by us on the refraction of gases, but the observations of Dulong on the vapours of water, bisulphide of carbon, and ether, and of Le Roux on the vapours of phosphorus and sulphur, afford the means of comparing the specific refractive energies of these substances when in a liquid and a gaseous condition. The results are given below, but, as a correction has been made of what appears to be an omission in Le Roux's method of calculation, a query is appended to the determinations of gaseous phosphorus and sulphur.

Condition.	Water.	Phosphorus.	Sulphur.	Bisulph. Carbon.	Ether.
Solid	·336	·58	·50	—	—
Liquid.....	·333	·59	·51	·49	·49
Gaseous	·321	·50?	·49?	·44	·46

From this table it would appear that while the specific refractive energy is the same in the solid and liquid condition, it is somewhat smaller in the gaseous. The differences may disappear on more close examination, but there seems reason to think, from the care that Dulong bestowed upon the matter, that, in reference to water at least, the difference is real.

Mixture and Solution.—With reference to mixture, the following was the conclusion arrived at by Mr. Dale and myself:—"The hypothesis that the specific refractive energy of a mixture of liquids is the mean of the specific refractive energies of its con-

stituents must stand as the nearest approximation to the truth." Landolt has confirmed this in a novel and interesting manner, by taking two organic liquids in certain equivalent proportions, mixing them, and comparing the specific refractive energy of the mixture with that of some organic liquid of the same ultimate atomic composition. He finds in seven recorded instances that the numbers are nearly identical, the refractive energy of the mixture being, however, always very slightly in excess. The most remarkable instance, perhaps, is that of a mixture of single equivalents of methylic alcohol and acetic acid, as compared with glycerin:

$$CH_4O + C_2H_4O_2 = C_3H_8O_3.$$

The following table of the refractive indices of alcohol of various strengths at 20° C. will serve to illustrate the effect of mixture, and all the better as a considerable contraction ensues, as is well known, on mixing alcohol with water:—

Liquid.			Density.	Refr. Index for A.	Spec. refr. energy.	Calculated mean.
Alcohol.		Water.				
100 parts		.....	0·797	1·3578	·448	—
90 „	+	10 parts.....	0·818	1·3593	·439	·436
50 „	+	50 „	0·915	1·3560	·389	·388
25 „	+	75 „	0·963	1·3455	·358	·358
		100	1	1·3285	·328	—

The numbers found by observation are as close to those deduced from theory as can be expected in experiments of this nature.

If a substance, in passing from a solid to a liquid state, does not change its specific refractive energy, it is to be expected that the laws of mixture will hold good equally whether both substances were originally liquid, or whether one of them was solid but had been liquefied by solution. And actual observation proves that this is the case. A solid substance when dissolved is found to have the same (or very nearly the same) specific refractive energy as it had previously; or, to speak more accurately, the specific refractive energy of a solution is the mean of the specific refractive energies of the solvent and the substance dissolved. The following table of solutions of sugar at 20 C. will illustrate this. The refractive index of crystallised cane-sugar is given on the authority of Brewster, its specific gravity on that of Thomson:—

Substance.	Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Sugar. Water.				
Whole	1·563	1·545	·349	—
66·6 parts + 33·3 parts	1·325	1·455	·343	·344
50 „ + 50 „	1·232	1·418	·339	·341
25 „ + 75 „	1·116	1·377	·337	·337
Whole	1	1·333	·333	—

This, however, is much more striking where there is a wide difference between the specific refractive energy of the solvent and that of the body dissolved. I became the possessor of a beautiful prism of rock-salt from Mr. J. G. Hofmann's case at the International Exhibition of 1862. Its refractive indices for the three principal lines of the spectrum were found to be—

A.	D.	H.
1·5369	1·5443	1·5685

Newton gave for rock-salt the index 1·545, Brewster 1·557. The refraction of pure chloride of sodium in a solid condition may be assumed as identical, or very nearly identical, with this; hence a solution was made of the chloride in three times its weight of water, and the refractive indices were taken. The following comparison will show that the salt in dissolving retains its original specific refractive energy :—

Substance.	Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Salt	2·086	1·544	·261	—
Solution	1·183	1·377	·318	·315
Water	1·	1·333	·333	—

The idea of solution need not be confined to the liquefaction of a solid. A gaseous body may carry its original specific refractive energy into its combinations with water; and that it sometimes does so (at least, within limits of possible experimental errors) is shown by the following observation on two solutions of ammonia, containing respectively 29·2 and 17·4 per cent. of the alkali. The observations on the gas are given on the authority of Dulong.

Substance.	Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Ammonia gas.....	0·00076	1·000385	·506	—
Solution, 29·2 p. c.....	0·8863	1·3491	·393	·383
„ 17·4 p. c.....	0·9338	1·3418	·366	·363
Water	1	1·333	·333	—

These instances might be multiplied from observations made by Mr. Dale and myself, and the refractive indices given by A. and E. Weiss* afford the means of similar calculations. The general result is that, as a rule, when a gas, liquid, or solid dissolves in water, it preserves its specific refractive energy; but that there are certain cases—as sulphuric acid—where the departure from what theory requires is too great to be attributed to errors of observation. There is one conclusion which is pretty safe, and may be of great value in future researches. When the refractive index of a strong solution is known, the refractive index of a more dilute solution may easily be reckoned from it, by making the proper allowance for the quantity of water added.

Chemical Combination.—Many of these cases of mixture or solution can scarcely be looked upon otherwise than as feeble chemical combinations. It might fairly be expected that the law which holds good with them would equally apply to some of those simpler combinations of elements, in which the physical properties of the compound do not differ very widely from those of its constituents united. It becomes indeed an interesting question to ascertain how far an element carries into its compounds its specific influence on the velocity of the rays of light.

The simplest cases of combination are where two elements combine, and do not change their aggregate condition, two gases for instance forming a compound gas, or two liquids a compound liquid. In regard to gases, the question was examined some time ago by Dulong, and, from a consideration of nine cases, he came to the conclusion that the refractive power of a gaseous compound is not the sum of the refractive powers of its gaseous constituents. He found it sometimes more, sometimes less; but after all the differences were not very large. It will be observed that Dulong did not compare the specific refractive energies $\frac{\mu - 1}{d}$, but what Newton

* Sitzungsberichte kais Akad. Wissensch. Math. Nat. 1858. xxxiii, 589.

termed the absolute refractive powers $\frac{\mu^2 - 1}{d}$; but though the difference between these formulæ is notable enough when they are applied to liquids or solids, they come to the same thing in the case of gases. This will be apparent from the following considerations:—

$$\mu^2 - 1 = (\mu - 1) \cdot (\mu + 1);$$

now, in a gas, μ consists of 1 followed by three zeros, as 1·000385; $\mu + 1$ therefore becomes a number scarcely exceeding 2, and the above equation amounts practically to

$$\mu^2 - 1 = 2\ (\mu - 1),$$

and the specific refractive energies of gases are simply half of their absolute refractive powers. Where, however, μ is such a number as 1·385, there is no such constant relation.

In calculating the theoretical specific refractive energy of a compound, it is necessary to multiply the energy of each constituent by the quantity of that constituent, add together the numbers so obtained, and divide the same by the quantity of the whole compound. But it is more convenient to adopt with Landolt what he terms the "molecular refractive energy," or "refraction-equivalent," that is, the specific refractive energy multiplied by the atomic weight, or $P\left(\frac{\mu - 1}{d}\right)$. Thus Dulong determined the refractive index (μ) of oxygen as 1·000272; and its specific gravity (d), on the scale of water being 1, is 0·00143. The specific refractive energy $\left(\frac{\mu - 1}{d}\right)$ is therefore ·190; and the refraction-equivalent is ·190 × 16, or 3·04. The refraction-equivalent of hydrogen gas, calculated from his numbers, is 1·53. Hence

	Refr. equiv.
2 atoms of hydrogen	3·06
1 atom of oxygen...	3·04
Sum.....	6·10

while the refractive equivalent of steam, calculated from Dulong's observations, is only 5·78. Before passing to another compound we may compare these numbers with the refraction-equivalents of

liquid and solid water, as deduced from their specific refractive energies given above :—

	Refr. equiv.
Sum of gases	6·10
Steam	5·78
Water	5·99
Ice.....	6·05

In our paper before the British Association, Mr. Dale and I gave the calculated and observed specific refractive energies of five liquid compounds, but the data were not published. One of these was terbromide of phosphorus, a liquid composed of two elements of which we had determined the refractive indices in the liquid condition.

Bromine permits only the extreme red rays to pass, but the lines A and B of the solar spectrum were perfectly visible, and the following determinations were made :—

	Line A.	Line B.
At 26° C.	1·6243	1·6333
At 35° C.	1·6150	1·6230

which would give for the refractive index of A at 20° C about 1·630; and taking the specific gravity of bromine at 2·98, we have

Specific refractive energy....	·212
Refraction-equivalent	16·9

The refraction-equivalent of melted phosphorus, reckoned from numbers previously given, is 18·3. We have therefore

	Refr. equiv.
1 atom of phosphorus.....	18·3
3 atoms of bromine.....	50·7
Sum	69·0

while the refraction-equivalent deduced from our observations on terbromide of phosphorus itself was only 63·4.

In bisulphide of carbon we have two elements solid at the ordinary temperature combining to form a liquid. The refraction-equivalent of carbon, as obtained from the diamond, is about 5·1 for the most luminous part of the spectrum : that of sulphur may

be taken at ·50 × 32, or 16·0 for the line D. We have therefore

	Refr. equiv.
1 atom of carbon.....	5·1
2 atoms of sulphur	32·0
Sum.....	37·1

The refraction-equivalent reckoned from the actual observations of bisulphide of carbon is 37·3—a very much nearer result than in the two cases previously discussed; indeed the numbers may be considered in this case as identical.

On comparing homologous series, Mr. Dale and I found that every increment of CH_2 caused an increase in the specific refractive energy (except in the case of the hydrocarbons), and we noticed that the amount of optical change was less between the higher than between the lower members of the series. Landolt shows that when the refraction-equivalents are compared, the difference is the same between each two consecutive members, and this difference he finds on an average to be 7·6. The actual numbers vary from 6·81 to 7·88, and the series he compared were the $C_nH_{2n}O_2$ acids, the alcohols, and certain compound ethers. On applying this mode of calculation to the series given in our previous paper, Landolt's conclusion is abundantly confirmed, not only in series commencing with iodide of methyl, formic ether, mercuric methyl, and hydride of œnanthyl, but also in the benzole and pyridine groups. The refraction-equivalent of olefiant gas, C_2H_4, reckoned from Dulong's numbers, is 15·09, which will give for the half CH_2, 7·54.

Landolt, by comparing the refraction-equivalents of liquids differing by a single atom of carbon, by two of hydrogen, or by one of oxygen, is able to show the influence which each of these elements exerts in their compounds, and by taking the following as the refraction-equivalents,

Carbon	=	5·0
Hydrogen	=	1·3
Oxygen	=	3·0

he is able to show a wonderfully close analogy between the calculated and the observed refraction-equivalents of a large number of liquids, all belonging, however, to the same class of organic com-

pounds, with indices ranging only from 1·328 to 1·471. The calculations given above from bisulphide of carbon and olefiant gas, and others that I have made from carbonic acid, the essential oils, and other substances, show the general uniformity of the action of the atoms of carbon on the rays of light, whether these atoms are crystallized together in the form of diamond, or are compounded with oxygen or hydrogen, sulphur or chlorine.

This mode of investigation may be applied to all the elements, and we have so applied it to a considerable number; but it would be premature to publish results, many of which rest on imperfect data. Some of the numbers which are given in this paper will probably have to be corrected. To determine the extent to which chemical combination may modify the specific refractive energies of the elements, and to ascertain the real value of these constants, requires that the refractive index and the density should be taken from the same specimen, that its purity should be guaranteed, that the part of the spectrum measured should be noted, and that the temperature should be mentioned, requisites not usually to be found in the recorded observations of refractive indices.

XXIV.—*Observations on some Points in the Analysis of Potable Waters.*

By Professor W. A. Miller, M.D., LL.D., Pres. Chem. Soc., Treas. and V.P.R.S.

(1.) Although the analysis of potable waters is an operation which every chemist has frequently occasion to perform, it is remarkable that there is much less agreement between different operators in the exact mode of conducting the details of the analysis, and of reporting the results than might have been expected. It is with the hope of contributing something towards facilitating greater uniformity in practice, and of adding precision to the results attained upon one or two important points, that I have been induced to bring the subject, trite as it may appear, before the Chemical Society on the present occasion.

I believe that much would be gained both in precision and in the comparability of our results, by performing every detail in

exactly the same way, time after time, as in the common methods of assaying. In such cases it is astonishing how closely the results obtained coincide with each other when the identical alloy is repeatedly subjected to the process by the operator, who may be, nevertheless, quite unconscious of the strictness of the ordeal which he is undergoing at the hands of the client who is testing the accuracy of his work. In a *résumé* of the nature of that which I am proposing to make on the present occasion, any great amount of novelty will not be expected. I have selected from every available source, with which I am acquainted, methods which, if not *minutely accurate* in the scientific sense of the word, experience has proved to be at least practically correct, and for the most part easy and rapid in performance.*

(2.) *Mode of observing Colour of a Water.*—After examining the *appearance* of the water in a beaker, a portion of it should be placed, as practised by Dr. Letheby, in a tube two feet in length and an inch or more in diameter, closed at the bottom with a flat plate of glass. A similar tube is filled with distilled water, and compared with the water under trial by placing the two tubes side by side, and looking down upon a white plate. The water usually has a shade of yellow, green, or brown if organic impurity be present, and the amount of colour can then be estimated and may be noted in terms of an arbitrary scale.†

(3.) *The amount of sediment* held in suspension in a gallon or half a gallon, or say three or five litres, is determined by allowing the water to settle, drawing off the clear water with a syphon, collecting the sediment on a weighed filter, and drying at 284° (140° C.); and the loss by ignition is afterwards ascertained when the filter and its contents are burned, and the residue is weighed.

(4.) *The taste* of a water, as was pointed out by Dr. T. Clark, should be determined both at the ordinary temperature and when it has been warmed to between 86° and 95° (30° and 35° C.), at which point any unpleasant flavour is much more distinctly perceptible than when the water is cool.

(5.) *The odour* will also be developed under similar circumstances, and will become more marked if a little lime or baryta-water be added before warming the water. It may be best ob-

* Since this paper was read, one or two alterations have been made in detail, in consequence of the remarks of friends, either at the meeting of the Chemical Society or in conversations since.

† If iron be present, special attention must be paid to this impurity.

served by placing a few ounces of the water in a flask partially filled, and drawing air through a tube from the upper part of the flask into one nostril, whilst the other is kept closed.

(6.) *The hardness of a water,* as determined by the soap-test of Dr. Clark, furnishes, of course, one of the most important data in relation to the fitness of such a water for domestic purposes; but all the particulars relating to the precautions needed to attain accuracy in this operation upon a water before it has been boiled have been so thoroughly worked out by Dr. T. Clark and Mr. D. Campbell, that I have nothing further to add. I may remark that in taking the hardness of a *boiled water,* a steady ebullition of not less than one hour should be maintained before determining the extent to which softening has been effected. The flask, of course, must contain a *weighed* quantity of water, and after the boiling the amount must be made up to the original weight by adding pure distilled water. A simple condenser, consisting of a tube about a third of an inch in diameter, four feet long, cut off obliquely below, and resting, by a bulb blown near its lower extremity, upon the neck of the flask, will reduce the loss by evaporation to an insignificant amount.

(7.) *Evaporation and Incineration.*—The most difficult, and at the same time most important, problem in the analysis of a water is the determination of the amount of the *organic matter,* as it is loosely termed, which it holds in solution. The plan often practised of simply evaporating down to dryness, weighing, and then igniting and weighing a second time, always leads to inexact results, and commonly produces an over estimate of the amount of organic matter, owing to the loss especially of hydrochloric acid and carbonic anhydride, if much magnesian salts are present.

It is better to add a known quantity of fused disodic carbonate (Na_2CO_3) to the vessel in which the evaporation is being effected. This evaporation is best performed in a platinum crucible capable of containing at least three ounces of water, and provided with a platinum cover. If it be intended to evaporate down two decigallons of the water, a known quantity, say four or five grains of disodic carbonate, should be added (or about 0·3 grm. of the carbonate to a litre of water). When the weight of the dry residue is ascertained, the amount of this carbonate is simply deducted from the weight obtained. Where the examination of several waters is in progress at once, the evaporations may be conveniently conducted in a copper steam-bath, in which they are

carried to apparent dryness. The drying must be completed in an air-bath, the temperature of which is maintained for one hour at about 284°, or not exceeding 302° F. (140° to 150° C.). The residue is then carefully weighed. The organic matter is afterwards burnt off at a red heat barely visible in daylight, and the residue when cold is again weighed. These weighings are more liable to error than any others during the analysis, and nowhere is an error of one or two hundredths of a grain more important. It is almost needless to say that the crucible must in each case be covered, and allowed to cool completely over a dish of sulphuric acid, and that the crucible must be introduced into the balance by means of tongs, as, if it be touched with the fingers, the warmth of the hand, by expanding the air contained within the covered crucible, would be liable sensibly to alter its weight. After the residue has been ignited, the saline mass must be moistened with a saturated solution of carbonic acid in distilled water, as first recommended by Dr. T. Clark. From two to three ounces of the carbonic acid solution should then be poured into the crucible. This solution must again be evaporated to dryness, and the residue maintained for one hour in the air-bath at the *same* temperature as that employed in the original desiccation. If any sensible amount of magnesian salts be contained in the water, the residue, after this treatment, will be found to have increased in weight by two or three tenths of a grain, when compared with the weight after simple incineration.

In this way we shall have ascertained the amount of the soluble constituents (both fixed and organic), as well as an approximative estimate of the amount of organic matter.

Nearly all waters, however, contain ammoniacal salts in minute quantity, and a variable amount of nitrates. The ammonia would of course escape as carbonate during the evaporation, but as the quantity of ammonia seldom exceeds a few thousandths of a grain per gallon, this introduces no error of importance. The nitrates would also remain nearly unchanged, even after ignition, unless the quantity of organic matter were considerable, when they would necessarily undergo decomposition more or less complete on incineration, and the loss of weight then observed would be due partly to this cause.

(8.) *Use of Potassic Permanganate.*—In the year 1850 Professor G. Forchhammer, of Copenhagen, proposed to employ a solution of potassic permanganate for the determination of the amount of organic matter in water (*Trans. Roy. Danish Society*, 5th series,

Physical and Mathem. section, vol. 2nd.) At the time, the method attracted but little attention, but recently many chemists have been induced to attempt to modify the process, and substitute its indications for the ambiguous results obtained by incineration. As a substitute it will probably fail, but as an accessory test it appears to be likely to render good service in assisting the judgment as to the salubrity of a water.

I have made a large number of experiments with the view of testing this method, and will now describe the plan which has succeeded in my hands.

A solution of potassic permanganate of convenient strength is first prepared; for this purpose the liquor may contain an amount of permanganate such that 10,000 water-grain measures shall in an acidulated solution exert an oxidizing power equal to that of one grain of oxygen, or 1 c. c. of liquid shall be equivalent to 0·1 milligramme of oxygen. For this purpose 3·95 grains of pure crystallised permanganate in 10,000 grains of water should suffice. This will be equivalent to 0 395 gramme of the salt in a litre of water; but its power may be exactly measured by means of a *freshly prepared* solution of crystallized oxalic acid containing 7·875 grains in 10,000 measured grains of water, or 0·7875 gramme of oxalic acid in 1 litre of water. 100 measures of this solution warmed with a very dilute solution of sulphuric acid should decolorize exactly 100 measures of the permanganate. 0·05 gall. (8 oz.) of each of the several waters for trial are then placed in a flask with 30 grains of undiluted hydrochloric acid, or 50 grains of diluted sulphuric acid (1 of acid to 3 of water); either acid may be used with equal advantage. The permanganate may then be added either in successive small doses till an excess is reached, or an excess may be added at once and the excess determined at the end of the experiment. Either plan will answer. If the method by gradual addition be preferred, to each flask must be added 20 grains of the permanganate solution, the flasks being arranged on a white ground side by side in front of a window: no artificial heat must be employed.* At intervals of 15 minutes the flasks are examined, and

* Two hundred and fifty cubic centimetres of the water with 2 c.c. of hydrochloric acid may be employed, and successive amounts of 0·5 c.c. of the permanganate solution may be used: on multiplying by 4 the number of cubic centimetres of permanganate employed, it will give the amount of oxygen in tenths of a milligramme required to oxidize the organic matter in each litre of water.

The solution of potassic permanganate, as well as the solution of dichromate, should be preserved in bottles, made of glass, free from lead.

successive quantities of 10 or of 5 grains of the permanganate solution are added, in proportion to the rapidity and completeness with which the colour disappears. These successive additions of the permanganate must be made until the last addition remains sensibly unaltered after the lapse of half an hour, which generally occurs between two and three hours from the commencement of the experiment. The number of water-grains of permanganate consumed in each case is then ascertained, deducting the last portion, which, it is estimated, remains unaltered in the flask. A little uncertainty occurs in estimating the amount of residual tint by the eye, and this occasions a variation of 2 or 3 divisions in different experiments. On multiplying by 20 the number of water-grains of permanganate solution consumed in each flask, we have the quantity of oxygen in ten-thousandths of a grain consumed in oxidizing the organic matter in one gallon of each sample of water.

The following table comprises the results of a series of trials with the same solution of permanganate, under varying circumstances, upon six different samples of acidulated water, and may serve as a specimen of the effects which such variations exert upon the amount of permanganate destroyed.—Temp. from 59° to 68° F. (from 15° to 20° C.).

	Permanganate added gradually.			Permanganate added in excess.						
	A.	B.	C.		E.	F.	G.	H.	I.	K.
1st water	41	41	40	4th water	16	15	15	14	13	—
2nd „	47	42	—	5th „	44	48	46	49	50	51
3rd „	35	35	—	6th „	45	45	47	43	47	43

Acid used in A, dilute sulphuric
„ „ B, hydrochloric
„ „ C, sulphuric
} Duration of experiment 2¾ hours.

This process may be simplified by adding at once an excess of the solution of permanganate, allowing the whole to stand for three hours, and then destroying the permanganate in excess by the addition of a reducing agent. Various reducing agents were at first tried unsuccessfully; amongst them were sulphurous acid, disodic sulphite, disodic hyposulphite, stannous dichloride and arsenious acid; but the results of repeated trials with the same water varied so much, that it was obvious this plan could not be relied on, partly owing to the action of the varying quantity of dissolved oxygen in the waters upon the reducing agent employed,

and partly owing to the difficulty of removing a certain residual brown tint, due to a compound of one of the intermediate oxides of manganese, which is commonly produced in waters rich in organic matter. When the water was originally mixed with the permanganate in excess, this brown tint disappears slowly, and only by using an excess of the reducing agent.

This difficulty, however, may be obviated, as suggested by Mr. V. Harcourt, by adding to the water, at the termination of the oxidizing action, a small quantity of a solution of potassic iodide and a little starch paste; the excess of permanganate or of manganic salt is by this means at once reduced to a manganous salt, and the amount of iodine liberated may be determined by the addition of a standard solution of disodic hyposulphite, which may be graduated by means of the solution of permanganate itself. For this purpose 10 grains of the crystallized hyposulphite when dissolved in 10,000 grains of water, or 1 gramme of the salt in a litre of water, will furnish a solution of convenient strength. The burette must be read off the instant the colour disappears, as on standing the blue tint returns.

The columns headed E, F, G in the table given above refer to three successive trials of the same three waters; 0·05 gallon was mixed in E with 50 grains of dilute sulphuric acid, and exposed for three hours at ordinary temperatures with 50 grains of permanganate solution. F, a similar and simultaneous experiment, but employing 70 grains of permanganate. G, a repetition of the experiment, using 100 grains of the solution of permanganate. H, I, K were three trials with the same waters on the following day, acidulating in the same manner as before. In H 80 grains of the permanganate solution was employed. I was a second trial with 100 grains; K, with 150 grains of permanganate.

The results of these and of numerous other experiments lead me to recommend that the permanganate be mixed in excess at once with the water acidulated with sulphuric acid, and that the experiment be continued without applying heat. At the end of three hours the excess of permanganate is to be determined by the aid of potassic iodide, starch, and disodic hyposulphite.

Various objections will naturally be raised to the use of the permanganate. It may be said, 1st, that the quantity of permanganate required will vary with the kind of organic matter, so that the bulk of liquid decolorized will not necessarily be proportioned to the weight of the organic substance present. 2nd. That certain

organic compounds may be absolutely or comparatively harmless, while an equal weight of some other organic body in active putrescence may be seriously deleterious, and that the permanganate does not distinguish between the two, so that a water which is comparatively harmless may even decolorize a larger amount of permanganate than another water containing a dangerous amount of some septic poison. 3rd. That bodies not organic—such, for instance, as the nitrites—will bleach the permanganate.

It may be replied that though this method by the permanganate is liable to these defects, yet that the very same objections apply with even greater force to the processes hitherto employed; and, further, that it is not improbable that the substances most readily oxidized are just those most likely to be injurious in their effects upon those who drink the water. Moreover, if nitrites are present, their action will be almost instantaneous, while that of the organic matter is gradual; besides which other tests will reveal the presence of nitrites.

(9.) *Gaseous Constituents.*—Conjointly with these observations on the action of the permanganate, it is of considerable importance to determine the gaseous contents of a water, and in particular the proportion of *dissolved* oxygen which it contains. I have already described in detail elsewhere an easy method of determining the amount of carbonic acid, oxygen, and nitrogen in a water, sufficiently accurate for this purpose (see my *Elem. Chem.* 3rd ed., vol. ii, pp. 40 and 60). For this purpose, however, it is necessary that the water be collected in glass stoppered bottles, filled as completely as possible; and the determination of the gaseous contents should be performed within twenty-four hours, or at least not more than forty-eight hours after the water has been collected.*

Whenever the proportion of oxygen is less than one-third that of the nitrogen, the water is to be looked upon as imperfectly aërated, the proportion in perfectly aërated water being, as is well known, owing to the superior solubility of oxygen, that of

* It is much to be wished that chemists would insist upon a greater uniformity in the way of collecting samples of water for analysis. Glass bottles, well stoppered, should alone be used for the purpose. Stoneware jars, which are often, but most improperly substituted for glass, should peremptorily be discarded. The stoneware is liable to introduce both calcic sulphate and common salt into the water. Persons who collect the samples of water should be instructed to rinse out the bottles thrice on the spot, and whenever it is practicable, to submerge the bottle completely in taking the specimen.

1 of oxygen to 2 of nitrogen. The proportion of carbonic anhydride in the mixed gas is determined by means of a concentrated solution of caustic potash, of sp. gr. 1·3, and the oxygen by the subsequent addition of pyrogallic acid (1 part of acid to 6 of water), as practised by Liebig.

(10.) *Estimation of Ammonia.*—The determination of ammonia is a point of importance, but it may be readily effected as follows:—Into a capacious retort a quart of the water is introduced, and the retort connected with a suitably-mounted Liebig's condenser; an ounce of baryta-water is then added, and 10 ounces of water are distilled over slowly. We may also use 1 litre of water, 25 c.c. of baryta-water, and distil over 250 c.c. of water. The residue in the retort is filtered and separated from barytic carbonate and sulphate, and then evaporated for subsequent determination of the nitrates by Pugh's method (par. 12). Too much care cannot be taken in conducting these experiments on the amount of ammonia, for owing to the condensation of ammoniacal salts upon glass vessels kept in a laboratory, unless much vigilance be exercised, an undue proportion of ammonia is liable to be reported.

The distillate is divided into two equal portions; one of these is submitted to Nessler's test for ammonia in the following manner, as practised by Mr. Hadow:—Make a concentrated solution of an ounce or more of corrosive sublimate; having dissolved $2\frac{1}{2}$ ounces of potassic iodide in about 10 ounces of water, add to this the mercurial solution until the iodide of mercury ceases to be dissolved on agitation; next dissolve 6 ounces of solid hydrate of potash in its own weight of water, and add it gradually to the iodized mercurial solution, stirring whilst the mixture is being made; then dilute the liquid with distilled water till it measures 1 quart. When first prepared, it usually has a brown colour of greater or less intensity, owing to the presence of a little ammonia; but, if set aside for a day or two, it becomes clear and nearly colourless; the clear liquid may then be decanted for use. For a litre of the test liquid of equal strength 62·5 grammes of potassic iodide and 150 grms. of solid caustic potash will be required. About 50 grains (3 c.c.) of this solution are drawn off by a marked pipette and added to one-half of the distillate; if no ammonia be present, the mixture remains colourless, but if ammonia be present, the liquid will assume a yellowish tinge of greater or less intensity. The

liquid will remain clear if the ammonia do not exceed one two hundredth of a grain in the 5 ounces, or about 0·25 mgm. in 125 grms. of the distillate. The quantity of ammonia in such a case may be very accurately estimated in the following manner:—A solution of sal-ammoniac is prepared containing 3·17 grains of the salt in 10,000 grains of water (or 0·317 grammes of salt per litre), which is equivalent to one ten-thousandth of a grain of ammonia (H_3N) in each grain of this solution, or 0·1 gramme in 1 litre. Suppose that a tint is obtained in the distilled liquid, which experience leads the observer to estimate, say at five thousandths of a grain; 50 grains of the standard sal-ammoniac solution are placed in a beaker, similar in size to that used for the distillate under trial, then diluted with 5 ounces of distilled water, previously ascertained to be free from ammonia (an impurity not unfrequently met with in the first portions of water which come over in distillation); lastly, 50 grains of the mercurial test-liquor are added.

If the tint coincides in intensity with that furnished by the distillate, which has received an *equal quantity* of the mercurial test, the amount of ammonia may be considered to correspond with that taken in the liquid for comparison. If the distillate appear to have a deeper or a paler tint, a second approximative trial with a larger or a smaller quantity of sal-ammoniac must be made, and so on until the operator is satisfied that the tints coincide. On multiplying the number of grains of sal-ammoniac solution employed by 8, the product will give, in ten-thousandths of a grain, the quantity of ammonia per gallon in the water under examination.* When the quantity of ammonia exceeds the 20th of a grain per gallon, or 0·6 mgm. per litre, it is necessary to determine the amount by neutralization; and it was to provide for this contingency that the second half of the ammoniacal distillate was directed to be reserved. A test acid composed of 2·882 grains of oil of vitriol in 1,000 of water, or 2·882 grammes H_2SO_4 diluted to 1 litre, will contain an

* Suppose that the observer estimates the amount of ammonia in the 125 c.c. on which he is operating at 0·25 mgrm., he takes 2·5 c.c. of the sal-ammoniac solution, and dilutes it with distilled water to 125 c.c.; he then adds 3 c.c. of the mercurial liquor, and compares it with the tint produced in the distillate by a like addition of the mercurial test. If the two tints correspond, multiply by 2 the number of c.c. of sal-ammoniac solution required, and the number obtained will give the proportion of ammonia per litre in tenths of a milligramme.

amount of acid, 1 grain of which will neutralize one ten-thousandth of a grain of ammonia, or 1 c.c., will be equivalent to 1 milligramme of H_3N. The neutralization is effected in the ordinary way, using infusion of litmus to indicate the point of transition from alkalinity to commencing acidity. During the separation of ammonia from the water by the distillation with baryta as above directed, it will often happen that some peculiar or characteristic odour is developed, which may be of importance as indicating some source of contamination which might otherwise be overlooked.

(11.) *Estimation of Nitrites.*—The presence of the alkaline nitrites in the well waters of towns is not unusual. The reaction of the nitrites upon potassic iodide and starch, employed by Dr. D. Price as a test for the iodides, may be used conversely to detect traces of the nitrites in waters, which it will reveal even when the amount of nitrite present is considerably less than a grain per gallon. It is merely necessary to add to a little dilute starch a few drops of a weak solution of potassic iodide, and then a few ounces of the water slightly acidulated with dilute sulphuric acid; an instantaneous blue coloration of the starch by liberated iodine will occur if the water contains any sensible amount of nitrite. The quantity of nitrites may be approximately estimated by the amount of a graduated solution of permanganate which a given measure of the water (say 0·05 gallon, or 250 c.c.) will bleach. When the solution of potassic permanganate is employed to determine the amount of organic matter, if nitrites be present, part of the permanganate will be destroyed by their action: the bleaching, though not absolutely instantaneous, takes place in a few seconds; and, therefore, it can be at once distinguished and measured separately from the reducing effect occasioned by the organic matter, which is always very gradual. The decoloration of 1 grain of a solution of permanganate of such strength as is described in paragraph 8, would represent 0·00237 grain of N_2O_3; or 1 c.c. would be equivalent to 0·237 milligramme of N_2O_3.

(12.) *Estimation of Nitrates.*—The method which may be conveniently employed for this purpose is that contrived by Dr. Pugh, (*Chem. Soc. Q. J.*, xii, p. 35), which, when the following precautions are observed, is very trustworthy and manageable. The liquid from which the ammonia has been expelled, as directed in paragraph 10, is filtered from the mixed barytic sulphate and carbonate, and is then concentrated by evaporation to about 1-50th

of its original bulk. About 30 grains (2 c.c.) of this liquid are then mixed with about an equal bulk of a strong solution of ferrous sulphate in a test-tube, and concentrated sulphuric acid is allowed slowly to flow down the inclined side of the tube, and, by the depth of brown coloration at the line of junction between the two liquids, the comparative richness in nitrates is roughly estimated. The quantitative determination may now be proceeded with. The standard solution of stannous dichloride may contain advantageously about 14 per cent. of the salt dissolved in a liquid containing about one-third of its bulk of ordinary hydrochloric acid of sp. gr. 1·150. A strong tube of hard glass, capable, when sealed up, of containing at least 130 grns. of water, or 8 c.c., is sealed securely at its lower extremity, drawn off to a strong capillary neck, and into it a given bulk, say 46 grain measures, or 3 c.c., of the tin solution is accurately measured by means of a pipette with a fine stem, not exceeding 1-10th inch in diameter. An equal bulk of the concentrated water is then measured in with the same precision, a small fragment of marble is introduced, and after effervescence has ceased, the capillary neck is drawn off and securely sealed. The tube is next to be exposed in an air-bath for 20 minutes to a heat of 340° F. (about 170° C.), and allowed to cool. The contents of the tube are then introduced into a beaker with 50 grains of hydrochloric acid and an ounce of water (or 3 c.c. hydrochloric acid and 30 c.c. water), a little starch paste, and a few drops of a solution of potassic iodide. To this mixture a solution of dipotassic dichromate ($K_2O.2CrO_3$) is added until the starch just indicates free iodine. In measuring off the solution, one of Mohr's burettes, graduated to divisions each equal to ten water grains, and provided with Erdmann's float, leaves nothing to be desired in volumetric accuracy. If the solution of dichromate be made to contain 7·277 grains of the salt in 1,000 grains of water, each grain of the solution will be equivalent to one-thousandth of a grain of nitric anhydride; and in like manner if 7·277 grammes of the salt be dissolved in a litre of water, every cubic centimetre will represent a milligramme of nitric anhydride (N_2O_5). An equal measure of the tin solution must be similarly tested; the difference in the number of grains of dichromate solution required in the two cases will give the number of thousandths of a grain of N_2O_5 present in the quantity of water submitted to experiment. If, for example, 1-5th gallon of water be concentrated to 280 grains, and 56 grains, or

1-5th of its bulk, be operated on, the amount employed represents that contained in the 25th part of a gallon, so that, if the amount of N_2O_5 obtained be multiplied by 25, it will give the amount per gallon. If the burette divisions each correspond to cubic centimetres, the quantity of N_2O_5 contained in the portion of concentrated water submitted to trial, will be given in milligrammes. The tubes, when carefully sealed, scarcely ever burst in this experiment when a sufficient space for the expansion of the liquid is allowed. If about 1-4th of the capacity of the tube be left free of liquid, the space is found to be ample.

(13.) *Lead.*—This impurity may be derived from leaden cisterns or service pipes. It is easily detected by acidulating with two or three drops of acetic acid, and adding to the water about 1-20th of its bulk of an aqueous solution of sulphuretted hydrogen. On looking down through a tube containing a column of water so prepared—10 inches in length, upon a white surface, and comparing with it a similar tube filled with the water without any addition, a brown discoloration more or less intense will be distinguished in the tube containing sulphuretted hydrogen, if lead be present; the amount of lead may be estimated by preparing a standard solution containing one ten-thousandth of its weight of lead, diluting the required quantity of this liquid with a known volume of distilled water, and comparing it with the water after the action of sulphuretted hydrogen, in a manner similar to that directed to be followed in the colour estimation of ammonia (par. 10). The standard lead solution may be prepared by dissolving 1·831 grain of normal crystallized lead-acetate in 10,000 of water, or 0·1831 gramme of the lead-salt in 1 litre of water.

(14.) *Determination of Saline Constituents.*—I have little that is new to add on this head respecting the actual quantitative estimation of the various constituents, but I should strongly recommend that in every case the amounts of the chlorine, sulphuric, nitric, and silicic anhydrides, the lime, magnesia, ammonia, potash, and soda, as actually obtained by experiment, should be given, as well as the weight of the earthy carbonates separated during ebullition. If the potash and soda are not estimated separately, their joint weight should be determined by precipitating the chlorine or sulphuric acid from the alkaline chlorides or sulphates. By reporting the results of our experiments in this way, and in this way only, is a strict comparison of the analytical results of different observers possible without much unnecessary labour.

On the representation of the exact form in which the different acids and bases are arranged in any water, chemists are not agreed, and it would be better to omit the practice of reporting the names of the salts altogether. If the plan thus recommended be adopted, the sum of the saline constituents would, of course, not correspond with the amount of fixed saline residue obtained on evaporation, but a general statement of the character of the water,—whether, for instance, calcareous, magnesian, or alkaline salts preponderated; whether carbonates, sulphates, or chlorides are most abundant,—would convey more real information to those who know little of chemistry than any enumeration of saline constituents, which no two chemists would report exactly in the same way.

Of course in all cases of importance each determination should be made in duplicate; a decigallon or a half-litre being quantities well suited to experimental work.

It is almost needless to say, that in all accurate experiments the precipitates should be collected upon filters which have been previously soaked in dilute nitric acid (1 part acid to 30 of water), and afterwards thoroughly washed in distilled water and dried.

It is obvious that the analysis must always be performed upon water absolutely freed from suspended matter, either by subsidence, which is best, or by filtration.

The *soluble silica* is determined in the usual manner from the portion of water (0·2 gallon, or 1 litre) evaporated down with disodic carbonate for fixed constituents. The ignited residue is treated with hydrochloric acid, adding distilled water, and then collecting the undissolved residue on a filter, igniting, and weighing.

The filtrate must be treated with a slight excess of ammonia, immediately filtered, and the precipitate thus separated will contain the *oxides of iron and manganese*, the *alumina*, and the *phosphates*. They may be reported together.

No direct determination of the quantity of *carbonic acid* which exists in combination with bases, can be conveniently practised, but the amount of mixed carbonates can be obtained with a fair approach to exactness by taking two Florence flasks—A and B—of similar size, counterpoising one against the other, and boiling down two decigallons of water in the flask A, concentrating to one-fourth of its bulk (or one litre boiled down to one-fourth), adding the water by degrees as it boils away. The ebullition

must, of course, be conducted with the usual precaution of inclining the flask so as to prevent loss by spurting.

The concentrated water must then be filtered upon a small weighed filter, washing out the loose portions of the carbonate into the filter, drying the flask A and adhering carbonates at 212° (100° C.), and sucking out the moist air, weighing when cold, counterpoising with the empty flask B, which should be placed alongside the flask A with the carbonates whilst it is cooling, the weighings being repeated as usual till after re-heating to 212° they become constant. The lime and magnesia in the precipitate can be estimated in the usual way if desired, and the deposited salts should be tested for sulphates, as a small quantity of calcic sulphate may occasionally be deposited if the quantity of sulphates be considerable.

It is easy to convert the report of the number of grains per gallon (70,000) into parts in 1,000,000 (or what amounts to the same thing, to milligrammes per litre), by dividing the result by 7, and multiplying by 100. If the quantities per litre have been obtained in milligrammes, the proportion in grains per gallon is given by the converse operation of dividing by 100 and multiplying by 7.

It may for the present be expedient, in accordance with popular usage, to continue to report the contents of the water per gallon, but the decimal report should never be omitted, as at no distant period we must anticipate that our insular prejudices in favour of our inconvenient system of weights and measures, will disappear before the manifest advantages of the decimal notation and the metrical system; and it certainly is to be expected from our men of science that by the adoption of the method in their reports to the public, they will facilitate and hasten its introduction. It is with the view of aiding in this respect that I have in this paper given the weights and measures on the English method, and also their equivalents on the metrical system, perhaps, in some measure, at the expense of succinctness, though I hope not of perspicuity.

In reporting a water, therefore, it might be convenient to sum up the results in some such form as the following:—

	Grains per gallon.	Parts per 1,000,000.
Appearance..		
Colour in two-foot tube		
Amount of sediment		
Containing { Combustible matter		
Containing { Inorganic residue		
Taste at 86° (30°C.)		
Odour		
Hardness on Clark's scale..		
Do. after boiling one hour..		
Oxygen absorbed by organic matter from permanganate		
Total solid contents		
Consisting of { Volatile and combustible matter ..		
Consisting of { Fixed salts		
Earthy carbonates		
The fixed salts containing { Chlorine		
The fixed salts containing { Sulphuric acid ($S\Theta_3$)		
The fixed salts containing { Nitric acid ($N_2\Theta_5$)		
The fixed salts containing { Soluble silica		
The fixed salts containing { Lime		
The fixed salts containing { Magnesia..		
The fixed salts containing { Oxides of iron and manganese, alumina, and phosphates		
The fixed salts containing { Potash $K_2\Theta$		
The fixed salts containing { Soda $Na_2\Theta$		
The fixed salts containing { Ammonia		
	Cubic inches per gallon.	Vols. in 1,000.
Total gases dissolved		
Consisting of { Carbonic acid ($C\Theta_2$)		
Consisting of { Oxygen		
Consisting of { Nitrogen..		
Ratio of oxygen to nitrogen		

XXV.—*Researches on Acids of the Acrylic Series.*—No. 1. *Transformation of the Lactic into the Acrylic Series of Acids.*

By E. Frankland, F.R.S., and B. F. Duppa, Esq.

The acrylic or oleic series of acids, represented as it is by a rather numerous list of members, has hitherto received a remarkably small share of the attention of chemists, and such is more especially the case as regards the constitution of these acids. This comparative neglect is doubtless due to the circumstance that these acids have hitherto maintained a very isolated position, having few points of attachment to other families of organic compounds, from which any probable hypothesis as to their internal architecture could be formed. We trust, however, that the opening of a new path admitting of ready access to this series will materially contribute to the completion of the history of these acids, especially as it discloses at the same time a view of their structure, which scarcely leaves any doubt regarding their atomic constitution.

Action of Terchloride of Phosphorus upon Ethylic Leucate or Diethoxalate.

When terchloride of phosphorus is gradually added to ethylic leucate, a considerable elevation of temperature takes place, and torrents of hydrochloric acid are evolved. The reaction is not, however, completed until the mixture has been submitted to upward distillation for several hours, during which operation a considerable quantity of amorphous phosphorus separates. As soon as the evolution of hydrochloric acid has ceased, the contents of the retort must be distilled nearly to dryness, and the distillate cautiously mixed with water. A layer of ethereal liquid collects on the surface, which, after repeated washing, first with water, and then with dilute solution of carbonate of soda, boils between 162° and 168° C.

Several ounces of ethylic leucate so treated, gave about two-thirds of its volume of this ethereal product. After drying with chloride of calcium, the greater part of it passed over on rectification at 165° C. It was perfectly free from chlorine, and yielded on analysis the following numbers:—

·2885 grm. burnt with oxide of copper, gave ·709 grm. carbonic acid, and ·2549 grm. water.

These numbers agree closely with the formula—

$$C_8H_{14}O_2,$$

as seen in the following comparison :—

	Calculated.		Found.
C_8	96	67·60	67·02
H_{14}	14	9·86	9·82
O_2	32	22·54	——
	142	100·00	

From considerations mentioned below, we regard this body as the ethylic ether of ethyl-crotonic acid, the latter consisting of crotonic acid in which one atom of hydrogen has been replaced by ethyl :

$C_4H_6O_2$	$C_4H_5(C_2H_5)O_2$
Crotonic acid.	Ethyl-crotonic acid.

Ethylic Ethyl-crotonate is therefore produced by the action of terchloride of phosphorus upon ethylic diethoxalate, according to the following equation :—

$$3\left\{\begin{matrix} C\left\{\begin{matrix} C_2H_5 \\ C_2H_5 \\ OH \end{matrix}\right. \\ C\left\{\begin{matrix} O \\ OC_2H_5 \end{matrix}\right. \end{matrix}\right. + PCl_3 = 3\left\{\begin{matrix} C\left\{\begin{matrix} C_2H_5 \\ C_2H_4'' \end{matrix}\right. \\ C\left\{\begin{matrix} O \\ O_2C_2H_5 \end{matrix}\right. \end{matrix}\right. + P\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. + 3HCl.$$

Ethylic diethoxalate. Ethylic ethyl-crotonate. Phosphorous acid.

Ethylic ethyl-crotonate is a colourless, transparent, mobile liquid, possessing a burning taste and a very penetrating odour, recalling at the same time the smell of oil of peppermint and that of mushrooms. It is almost insoluble in water, to which, however, it communicates its peculiar taste and odour in a very high degree. Alcohol and ether dissolve it in all proportions. Its specific gravity is ·9203 at 13° C. It does not oxidize on exposure to air, and is not decomposed by water. Ethylic ethyl-crotonate boils at 165° C., and distils without decomposition. A determination of its vapour density by Gay-Lussac's method gave the following data :—

Weight of ethylic ethyl-crotonate	·1725 grm.
Observed volume of vapour..	54·66 cbc. c.
Temperature of bath	190° C.
Height of barometer	752 m.m.
Height of mercury inside of tube above that outside	94·5 m.m.
Equivalent of spermaceti column in millimetres of mercury	15·7 m. m.

From these data the specific gravity was calculated to be 4·83, the theoretical number for a two-volume vapour (H_2O = 2 vols.) of the above formula being 4·90.

Boiled with alcoholic potash, ethylic ethyl-crotonate is completely decomposed, yielding alcohol and potassium ethyl-crotonate. After treating the solution with water, and evaporating off the alcohol, the potassium ethyl-crotonate was treated with excess of sulphuric acid and submitted to distillation. An oily liquid, together with a large quantity of water, passed over and solidified before leaving the condenser, which required to be kept warm to prevent its being obstructed by the crystalline product. The whole of the distillate on being warmed, presented the appearance of a colourless oil floating on the surface of water, and on cooling, the oily layer solidified to a mass of splendid crystals, some of which were continued downwards through the water to the depth of 4 inches. These crystals, after pressing between folds of blotting paper and drying over sulphuric acid in vacuo, are specifically heavier than water, although the oil which they form when melted floats upon that liquid. They gave the following analytical results:—

·2524 grm. gave ·5799 grm. carbonic acid, and ·2002 grm. water.

These numbers correspond well with those calculated from the formula of ethyl-crotonic acid,

$$C_2\begin{cases} C_2H_5 \\ C_2H_4'' \\ \hline O \\ OH \end{cases}$$

	Calculated.		Found.
C_6	72	63·15	62·66
H_{10}	10	8·77	8·81
O_2	32	28·08	——
	114	100·00	

Ethyl-crotonic acid crystallises very readily from fusion in large and brilliant quadrilateral prisms, which melt at 39·5° C., and possess a peculiar odour, somewhat resembling that of a mixture of pyrogallic acid and benzoic acids. It sublimes at ordinary temperatures, is very soluble in alcohol and ether, but sparingly so in water. Its aqueous solution reddens litmus powerfully, and neutralises the strongest bases. The salts of ethyl-crotonic acid are generally distinguished by the facility with which they become basic on the evaporation of their solutions. The potassium, sodium, and barium salts are of a soapy nature, especially the two former, which separate from their concentrated solutions, and float on the surface. The silver, copper, and lead salts are very sparingly soluble in water.

Silver Ethyl-crotonate is obtained as a white crystalline precipitate, by mixing tolerably concentrated solutions of ammonium ethyl-crotonate and silver nitrate. Thrown upon a filter, well washed with water, and then dried in vacuo, it yielded on analysis the following numbers :—

I. ·4022 grm. gave ·4796 grm. carbonic acid and ·1464 grm. water.

II. ·3380 grm. gave ·1654 grm. metallic silver.

The following comparison shows that these numbers agree closely with the formula—

$$C_2\left\{\begin{matrix} C_2H_5 \\ C_2H_4'' \\ O \\ OAg. \end{matrix}\right.$$

	Calculated.		I.	II.
C_6	72	32·58	32·52	——
H_9	9	4·07	4·05	——
O_2	32	14·48	——	——
Ag	108	48·87	——	48·93
	221	100·00		

Silver ethyl-crotonate crystallises from water in minute scales, which are only slightly discoloured by light, or by a temperature of 100° C. By boiling, or even by evaporation of its solution over sulphuric acid in vacuo, this salt loses acid; a specimen so obtained in vacuo gave on analysis 30·78 per cent. of carbon, 4·04 of hydrogen, and 49·95 per cent. of silver.

Cupric Ethyl-crotonate is readily obtained as a beautiful greenish blue precipitate, by adding a solution of cupric sulphate to one of ammonium ethyl-crotonate. This precipitate, well washed, and afterwards dried in vacuo, gave the following analytical results:—

I. ·3052 grm. gave ·5442 grm. carbonic acid and ·1748 grm. water.

II. ·2127 grm. gave ·0570 grm. cupric oxide.

These numbers correspond sufficiently with those calculated from the formula

$$C_4\begin{cases}(C_2H_5)_2\\(C_2H_4'')_2\\\hline O_2\\O\\O\,Cu''\end{cases}$$

	Calculated.		Found.	
			I.	II.
C_{12}	144	49·74	48·63	——
H_{18}	18	6·22	6·36	——
O_4	64	22·11	——	——
Cu	63·5	21·93		21·41
	289·5	100·00		

The deficiency in the amount of carbon in the above analysis is doubtless due to the extreme facility with which this salt loses acid. A sample, which had been boiled for only a few minutes, gave 43·54 per cent. of carbon, 5·66 of hydrogen, and 27·07 per cent. of copper.

Lead Ethyl-crotonate was prepared by mixing solutions of lead acetate and ammonium ethyl-crotonate. It falls as a brilliant white curdy precipitate, which is perfectly insoluble in water. Submitted to analysis, ·4265 grm. gave ·5149 grm. carbonic acid, ·1647 grm. water, and ·2169 grm. lead oxide; numbers which closely correspond with the formula

$$C_4\begin{cases}(C_2H_5)_2\\(C_2H_4'')_2\\\hline O_2\\O\\O\,Pb''\end{cases}$$

as is seen from the following calculation:—

	Calculated.		Found.
C_{12}	144	33·26	32·93
H_{18}	18	4·16	4·29
O_4	64	14·78	15·58
Pb	207	47·80	47·20
	433	100·00	100·00

Action of Potassic hydrate upon Ethyl-crotonic Acid.

When ethyl-crotonic acid is mixed with a large excess of potassic hydrate and heated to about 180° C., hydrogen gas is evolved in large quantity, and the residual mass, when treated with water and excess of sulphuric acid, gives an acid distillate, which, by Liebig's process of semi-saturation, is completely resolved into two acids; the silver salt of one of these yielded on analysis the following results:—

·2904 grm. gave ·2599 grm. carbonic acid, ·0959 grm. water, and ·1613 grm. metallic silver.

These numbers shew that this salt is silver butyrate, as seen from the following comparison of the experimental with the calculated percentage quantities:—

	Calculated.		Found.
C_4	48	24·61	24·41
H_7	7	3·59	3·67
O_2	32	16·42	16·38
Ag	108	55·38	55·54
	195	100·00	100·00

The silver salt of the second acid is silver acetate; it crystallises in needles, which left on incineration 63·82 per cent. of silver. Silver acetate contains 64·64 per cent. Ethyl-crotonic acid is therefore decomposed by potassium hydrate into the potassium salts of butyric and acetic acids, with evolution of hydrogen, according to the following equation:—

$$C_2\left\{\begin{matrix}C_2H_5\\C_2H_4''\\O\\OH\end{matrix}\right. + 2KHO = C_2\left\{\begin{matrix}C_2H_5\\H_2\\O\\OK\end{matrix}\right. + C_2\left\{\begin{matrix}H_3\\O\\OK\end{matrix}\right. + H_2$$

Ethyl-crotonic acid. Potassium butyrate. Potassium acetate.

These are also the results of the action of the same reagent upon pyroterebic acid, which is isomeric with ethyl-crotonic acid. The cause of this identity of products from isomeric compounds we have explained below.

Action of Terchloride of Phosphorus upon Ethylic Ethomethoxalate.

When ethylic ethomethoxalate is treated with terchloride of phosphorus, the same phenomena are observed as in the corresponding reaction just described. After the complete cessation of the evolution of hydrochloric acid, the liquid was distilled, and the distillate washed, first with water, and then with dilute solution of sodium carbonate. An ethereal liquid separated as before, which, after drying over chloride of calcium, was submitted to rectification. We have not analytically proved the composition of this ether, but from the mode of its formation and the result of its decomposition by alcoholic potash, there can be no doubt that it is homologous with ethylic ethyl-crotonate, and that its formula is

$$C_7H_{12}O_2.$$

The same considerations which led us to regard the ethereal product of the previous reaction as ethylic ethyl-crotonate demand for this ether, the name *ethylic methyl-crotonate,* and the formula

$$C_2\left\{\begin{matrix}CH_3\\C_2H_4''\\O\\OC_2H_5\end{matrix}\right.$$

Ethylic methyl-crotonate is a colourless, transparent, mobile liquid, boiling at 156° C., possessing an insupportable and very persistent odour of decaying mushrooms, and a burning taste. It is lighter than, and nearly insoluble in, water. Alcohol and ether dissolve it in all proportions. Treated with boiling alcoholic potash, it is readily decomposed, yielding alcohol and potassium methyl-crotonate. An aqueous solution of the latter, mixed with excess of dilute sulphuric acid, and submitted to distillation, yields a beautifully crystalline body, which is methyl-crotonic acid,

$$C_2\left\{\begin{matrix}CH_3\\C_2H_4''\\O\\OH\end{matrix}\right.$$

Methyl-crotonic acid fuses at 62° C., and crystallizes on cooling

in splendid needles, which are considerably more soluble in water than ethyl-crotonic acid. It possesses the same aromatic odour as ethyl-crotonic acid, but more intense, and in its other properties closely resembles the latter. Its salts have a strong tendency to become basic on the evaporation of their solutions. We have examined the barium and silver salts.

Barium Methyl-crotonate is readily obtained by adding barium carbonate to a hot solution of methyl-crotonic acid, filtering and evaporating in vacuo over sulphuric acid. The salt which separates is difficultly crystallisable; dried in vacuo it gave on analysis 39·90 per cent. of barium. The formula—

$$C_4\begin{cases}(CH_3)_2\\(C_2H_4'')_2\\\hline O_2\\O\\O\end{cases}Ba''$$

requires 40·89 per cent. of barium. Barium methyl-crotonate is very soluble in water.

Silver methyl-crotonate is best prepared by precipitating a moderately concentrated solution of barium methyl-crotonate with nitrate of silver. The silver methyl-crotonate falls as a white crystalline powder, which is little affected by light, and very slightly soluble in water. Well washed with water and dried in vacuo, ·2246 grm. gave, when burnt with oxide of copper, ·2417 grm. carbonic acid, ·0735 grm. water, and ·1167 grm. metallic silver. These numbers agree sufficiently with the formula

$$C_2\begin{cases}CH_3\\C_2H_4''\\\hline O\\OAg\end{cases}$$

as is seen from the following calculation:—

	Calculated.		Found.
C_5	60	28·99	29·35
H_7	7	3·38	3·63
O_2	32	15·46	15·06
Ag	108	52·17	51·96
	207	100·00	100·00

Action of Potassium Hydrate upon Methyl-crotonic Acid.

Heated with an excess of potassium hydrate, methyl-crotonic acid evolves abundance of hydrogen, and the residue yields, on distillation with dilute sulphuric acid in excess, an acid mixture, which the process of fractional saturation resolves into propionic and acetic acids. The barium salts of these acids yielded respectively 47·86 and 51·97 per cent. of barium. The formula of barium propionate requires 48·41 per cent., and that of barium acetate 52·73 per cent of barium.

Methyl-crotonic acid is therefore decomposed by potassium hydrate into propionic and acetic acids, with the evolution of hydrogen, according to the following equation :—

$$C_2\begin{cases}CH_3\\ C_2H_4''\\ O\\ OH\end{cases} + 2KHO = C_2\begin{cases}CH_3\\ H_2\\ O\\ OK\end{cases} + C_2\begin{cases}H_3\\ \\ O\\ OK\end{cases} + H_2$$

Methyl-crotonic acid. Potassium propionate. Potassium acetate.

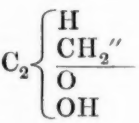
These results of the action of potassium hydrate upon methyl-crotonic acid are identical with those obtained by Chiozza in acting the same reagent upon angelic acid,* with which methyl-crotonic acid is isomeric. They show that the conversion into water, of the atom of peroxide of hydrogen in ethylic ethomethoxalate, is effected at the expense of the constitutional ethyl exclusively, the methyl remaining intact.

Action of Terchloride of Phosphorus upon Ethylic Dimethoxalate.

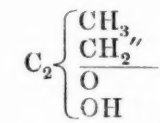
Ethylic dimethoxalate is readily attacked by terchloride of phosphorus, even at ordinary temperatures, but to complete the reaction it is necessary to heat the mixture to ebullition in a flask, with an inverted condenser, for several hours, taking care to employ a large excess of the terchloride. When the evolution of hydrochloric acid has completely ceased, the contents of the flask may be distilled from an oil-bath nearly to dryness, the distillate mixed cautiously with water, and the ethereal layer floating on the surface removed by decantation. After washing with water and solution of carbonate of soda, drying over chloride of calcium

* Ann. Ch. Phys. [3], xxxix, 435.

and rectification, the new ether possesses the following properties. It is a colourless, transparent, and very mobile liquid, having the nauseating odour of decaying mushrooms in a very high degree. This odour becomes more powerful as the atomic weight of these ethers is lowered, and reaches its climax in the body we are now describing. From the mode of its formation and the composition of the acid obtained from it, there can be no doubt that this ether possesses the composition of ethylic crotonate, but the decomposition which the acid suffers when heated with potassium hydrate, proves that it is metameric, and not identical with ethylic crotonate. We shall state at the conclusion of this paper our reasons for regarding this ether as the ethylic salt of methacrylic acid, the latter being acrylic acid in which an atom of hydrogen has been replaced by methyl—



Acrylic acid.



Methacrylic acid.

Ethylic methacrylate is readily decomposed by boiling alcoholic potash, yielding alcohol and the potassium salt of methacrylic acid, which crystallises from the alcoholic solution in beautiful scales. Distilled with excess of dilute sulphuric acid, potassium methacrylate yields methacrylic acid, which at first separates as an oily layer on the surface of the distillate, but afterwards dissolves in the water, which passes over with it.

Methacrylic acid is a colourless oil, which does not solidify at 0° C., and possesses a faint odour, like pyrogallic acid. It has a powerful acid reaction, and its salts have the same tendency to lose acid by evaporation, as those of the other members of the acrylic family.

Silver methacrylate is best obtained pure by precipitating ammonium methacrylate with nitrate of silver. It falls as a white precipitate, but slightly soluble in water, and not much affected by light. After washing and subsequent drying in vacuo over sulphuric acid, ·3038 grm. of this salt gave, on combustion with oxide of copper and free oxygen, ·2785 grm. carbonic acid, ·0780 grm. water, and ·1705 grm. metallic silver, numbers which correspond closely with those calculated from the formula

$$C_2\begin{cases} CH_3 \\ CH_2'' \\ \hline O \\ OAg \end{cases}$$

	Calculated.		Found.
C_4	48	24·87	25·00
H_5	5	2·59	2·85
O_2	32	16·54	16·03
Ag	108	56·00	56·12
	193	100·00	100·00

Barium methacrylate is very soluble in water, and on the evaporation of its solution, either in vacuo or by heat, it solidifies to a transparent gum-like mass.

Cupric methacrylate, unlike its isomer, cupric crotonate, is tolerably soluble in water.

Action of Potassium Hydrate upon Methacrylic Acid.

When methacrylic acid is heated with excess of potassium hydrate, nearly to the temperature of boiling oil, much hydrogen is given off, and the residual mass, on distillation with dilute sulphuric acid, gives an acid distillate, which, boiled with mercuric oxide, does not reduce the latter, thus proving the absence of formic acid. The acid distillate was converted into a silver salt, and dried in vacuo. ·3163 grm. of this salt gave on analysis, ·2299 grm. carbonic acid, ·0802 grm. water, and ·1874 grm. metallic silver. The salt was therefore propionate of silver, as will be seen from the following comparison of calculated and experimental numbers:—

	Calculated from $C_3H_5AgO_2$.		Found.
C_3	36	19·89	19·83
H_5	5	2·76	2·82
O_2	32	17·68	18·10
Ag	108	59·67	59·25
	181	100·00	100·00

Heated with potassium hydrate, therefore, methacrylic acid is transformed, with evolution of hydrogen, into propionic and formic acids, according to the following equation:

$$C_2\begin{cases}CH_3\\CH_2''\\\underline{\quad O\quad}\\OH\end{cases} + 2KHO = C_2\begin{cases}CH_3\\H_2\\\underline{\quad O\quad}\\OK\end{cases} + C\begin{cases}H\\O\\OK\end{cases} + H_2$$

Methacrylic acid. Potassium propionate. Potassium formate.

The absence of formic acid from the acid distillate is by no means incompatible with the foregoing explanation of the reaction, and need not create surprise, when it is remembered that this acid is readily converted into oxalic acid, with evolution of hydrogen, on being heated with potassium hydrate; and it must also be mentioned that the temperature required for this decomposition of methacrylic acid is much higher than that necessary for either ethyl or methyl-crotonic acid. Although oxalic acid is, in turn, also converted into carbonic acid, with evolution of hydrogen, by the same agent, at a more elevated temperature, still we expected to find at least traces of oxalic acid amongst the products of decomposition; but in this we were disappointed, and it therefore became necessary to examine the behaviour of formic acid itself, under the influence of an excess of potassium hydrate at the same temperature. We also simultaneously exposed oxalic acid with excess of potassium hydrate in the same bath. The latter acid was not in the least acted upon at the temperature employed for the decomposition of methacrylic acid; on the other hand, a very copious evolution of hydrogen took place from the formic acid, the residual product of which did not, however, at the conclusion of the reaction, contain a trace of oxalic acid. It is therefore evident that, at the temperature necessary for the decomposition of methacrylic acid by potassium hydrate, formic acid itself is converted at once into carbonic acid without any intermediate formation of oxalic acid.

This result of the action of potassium hydrate upon methacrylic acid proves the isomerism of the latter with crotonic acid, which yields under the same treatment acetic acid only.

Action of Terchloride of Phosphorus upon Ethylic Lactate.

If the reactions described in the foregoing pages were homologously continued to ethylic lactate, there ought to be produced ethylic acrylate, according to the following equation :—

$$3C_2\left\{\begin{matrix}H\\CH_3\\OH\\\hline O\\OC_2H_5\end{matrix}\right. + P'''Cl_3 = 3C_2\left\{\begin{matrix}H\\CH_2''\\\hline O\\OC_2H_5\end{matrix}\right. + P'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. + 3HCl$$

Ethylic-lactate. Ethylic acrylate.

There is, however, frequently a difficulty in carrying a general reaction of this nature to the extreme lower limit of the series; thus, for instance, the reactions for the production of ketones and anhydrides cannot be extended to formic acid, and we were therefore not altogether unprepared for failure, in attempting the production of acrylic from lactic ether. We find, in fact, that this reaction, sharp and definite as it is in the case of diethoxalic, ethomethoxalic, and dimethoxalic ethers, fails utterly when attempted with ethylic lactate or methydroxalate.

When terchloride of phosphorus is added to ethylic lactate, the action is even more energetic than in the former cases, and torrents of hydrochloric acid are evolved, in fact, to all appearance, the action is the same as with the other ethers of the lactic family; but on separating and purifying the ethereal product, as before, it is found to burn with a green-fringed flame, characteristic of the presence of chlorine. Submitted to analysis, this ether gave the following results:—

·2889 grm. gave ·4598 grm. carbonic acid and ·1736 grm. water.

These numbers agree closely with those calculated from the formula of ethylic chloropropionate, first prepared by Wurtz, from lactyl chloride and sodium ethylate, as seen from the following comparison:—

	Calculated from $C^3H^4Cl(C^2H^5)O^2$		Found.
C_5	60	43·95	43·41
H_9	9	6·59	6·68
Cl	35·5	26·01	
O_2	32·0	23·45	
	136·5	100·00	

The ether has the same boiling point (144° C.) as Wurtz's compound, and is in every respect apparently identical with it. The formation of ethylic chloro-propionate in the above reaction

is explained by the following equation, which, however, does not take cognizance of the hydrochloric acid which was evolved:—

$$3C_2\begin{cases} H \\ CH_3 \\ OH \\ \overline{O} \\ OC_2H_5 \end{cases} + PCl_3 = 3C_2\begin{cases} H \\ CH_3 \\ Cl \\ \overline{O} \\ OC_2H_5 \end{cases} + P\begin{cases} OH \\ OH \\ OH \end{cases}$$

Ethylic lactate. Ethylic chloropropionate.

There can be little doubt that the single atom of hydrogen in ethylic lactate plays an important, though unknown, part in this reaction; and it is not improbable that, in the first instance, this atom of hydrogen is removed along with peroxide of hydrogen, from the ethylic lactate, and escapes as hydrochloric acid. The exigencies of atomicity, however, require that the place of this hydrogen should be occupied by some other monatomic body: this is probably a compound of phosphorus, the presence of a considerable quantity of which in the crude ether was proved. The ultimate production of ethylic chloro-propionate may be explained on the assumption that this phosphorus compound becomes again replaced by hydrogen, during the subsequent washing of the ether. This point, however, we hope to elucidate in a future communication.

In connection with this reaction, we have to mention that phosphoric anhydride appears to dehydrate the ethers of the lactic series, in the same manner as terchloride of phosphorus. Thus ethylic dithoxalate is at once transformed into ethylic ethyl-crotonate, when it is gently heated with phosphoric anhydride, the reaction being:—

$$2C_2\begin{cases} C_2H_5 \\ C_2H_5 \\ OH \\ \overline{O} \\ OC_2H_5 \end{cases} + P_2''O_5 = 2C_2\begin{cases} C_2H_5 \\ C_2H_4'' \\ \overline{O} \\ OC_2H_5 \end{cases} + 2P''\begin{cases} O \\ O \\ OH \end{cases}$$

Ethylic diethoxalate. Ethylic ethyl-crotonate.

We are not without hopes that by the application of this reagent to lactic ether, we shall be able to transform the latter into acrylic ether.

The Relations of the Artificial to the Natural Acids of the Acrylic Series.

In the foregoing pages we have described the transformation of three synthesized acids of the lactic, into acids of the acrylic series. We have indicated that these transformed acids are isomeric, and not identical with certain natural acids of the same composition; but it is now necessary that we should inquire somewhat more minutely into the relations existing between the transformed and natural acids, and into the cause of their isomerism.

If the formula of acrylic acid given above be examined, it will be found that this acid must be the lowest possible term of the series, and that it is incapable of isomeric change, unless an alteration in the position of the atoms, with regard to the grouping carbon, determines such isomerism—an assumption which is at present totally unsupported by facts. It is, therefore, certain that acrylic acid is incapable of isomeric modification from a change in the composition of its constituent radicals.

By heating with potassium hydrate, acrylic acid, as is well known, yields acetic and formic acids, with evolution of hydrogen, according to the following equation:—

$$C_2\begin{cases}H\\ CH_2''\\ O\\ OH\end{cases} + 2KHO = C_2\begin{cases}H_3\\ \\ O\\ OK\end{cases} + C\begin{cases}H\\ O\\ OK\end{cases} + H_2$$

This mode of decomposition assumes the simple replacement of diatomic methylene by two atoms of hydrogen, the expelled methylene being at the same time oxidized to formic acid. But there is also another and by no means improbable mode of viewing this reaction, viz., that the molecule of acrylic acid is entirely broken up by the separation of the two dominant atoms of carbon, in fact, by a transformation of the hexatomic into the tetratomic carbon type, according to the equation:—

$$C_2\begin{cases}H\\ CH_2''\\ O\\ OH\end{cases} + 2KHO = C\begin{cases}H\\ O\\ OK\end{cases} + C\begin{cases}CH_2 + H\\ \\ O\\ OK\end{cases} + H_2$$

Acrylic acid. Potassium formate. Potassium acetate.

It is impossible to decide between these views, so long as the two radicals above the horizontal line of the formula differ by one

atom of carbon, as in the case of acrylic and methyl-crotonic acids.

$$C_2\left\{\begin{matrix}H\\CH_2''\\O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}CH_3\\C_2H_4''\\O\\OH\end{matrix}\right.$$

Acrylic acid. Methyl crotonic acid.

Both these acids would exhibit with potassium hydrate exactly the same products of decomposition, no matter which view of the reaction be the correct one, acrylic acid yielding acetic and formic acids, whilst methyl-crotonic acid would give, under both schemes of decomposition, acetic and propionic acids. Fortunately, however, the behaviour of an acid in which both the radicals just alluded to contain an equal number of carbon atoms, definitely decides between the two hypotheses. Two such acids synthetically prepared, and the nature of whose atoms is therefore known, have been described above, viz., ethyl-crotonic and methacrylic acids.

$$C_2\left\{\begin{matrix}C_2H_5\\C_2H_4''\\O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}CH_3\\CH_2''\\O\\OH\end{matrix}\right.$$

Ethylcrotonic acid. Methacrylic acid.

According to the view which assumes the conservation of the hexatomic type of the original acid, ethyl-crotonic acid ought to yield, by heating with potassium hydrate, butyric and acetic acids, whilst methacrylic acid should give, under like conditions, propionic and formic acids. We have already proved that these are actually the products obtained from these acids. But if the view which assumes the change from the hexatomic to the tetratomic type were correct, then ethyl-crotonic acid ought to yield two atoms of propionic acid; and in like manner methacrylic acid should give two atoms of acetic acid, according to the following equations:—

$$C_2\left\{\begin{matrix}C_2H_5\\C_2H_4''\\O\\OH\end{matrix}\right. + 2KHO = C\left\{\begin{matrix}C_2H_5\\O\\OK\end{matrix}\right. + C\left\{\begin{matrix}C_2H_4+H\\O\\OK\end{matrix}\right. + H_2$$

Ethyl-crotonic acid. Potassium propionate. Potassium propionate.

$$C_2\left\{\begin{matrix}CH_3\\ CH_2''\\ \overline{O}\\ OH\end{matrix}\right. + 2KHO = C\left\{\begin{matrix}CH_3\\ O\\ OK\end{matrix}\right. + C\left\{\begin{matrix}CH_2+H\\ O\\ OK\end{matrix}\right. + H_2$$

Methacrylic acid. Potassium acetate. Potassium acetate.

Having thus definitely established the nature of the reaction which takes place when the acids of the acrylic series are heated with potassium hydrate, we can now apply the information so acquired for the purpose of determining the constitution of those natural acids of this series, besides acrylic acid, whose products of decomposition have thus been determined, viz., crotonic acid, angelic acid, pyroterebic acid, and oleic acid.

For crotonic acid the two following formulæ are alone possible :—

$$C_2\left\{\begin{matrix}H\\ C_2H_4''\\ \overline{O}\\ OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}CH_3\\ CH_2''\\ \overline{O}\\ OH\end{matrix}\right.$$

and of these the first only could be made to exhibit the products of decomposition yielded by that acid when treated by potassium hydrate. Hence crotonic acid contains, as basylous radicals, hydrogen and ethylene, and hence the names which we have applied to the two homologous synthesized acids, methyl-crotonic and ethyl-crotonic acids, the products of whose decomposition by potassium hydrate prove them to contain respectively ethyl and methyl in the place of the hydrogen-radical of crotonic acid.

$$C_2\left\{\begin{matrix}CH_3\\ C_2H_4''\\ \overline{O}\\ OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}C_2H_5\\ C_2H_4''\\ \overline{O}\\ OH\end{matrix}\right.$$

Methyl-crotonic acid. Ethyl-crotonic acid.

As we ascend the series, the number of possible metameric acids increases, and the next higher compound, angelic acid, admits of being expressed by three formulæ, viz. :—

$$C_2\left\{\begin{matrix}H\\ C_3H_6''\\ \overline{O}\\ OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}CH_3\\ C_2H_4''\\ \overline{O}\\ OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}C_2H_5\\ CH_2''\\ \overline{O}\\ OH\end{matrix}\right.$$

Of these the first only can be the rational formula of angelic acid,

because that acid yields, when heated with potassium hydrate, propionic and acetic acids, which excludes the third of the above formulæ. The two remaining formulæ both exhibit the same results, when they are used in an equation representing the action of potassium hydrate upon this acid; but one of these formulæ, viz., the second, is known by synthesis to be that of methyl-crotonic acid, from which angelic acid differs by 17° C. in its melting point, the former melting at 62° C., whilst the latter fuses at 45° C. Hence, unless unknown causes of isomerism be assumed,

$$C_2\left\{\begin{matrix}H\\C_3H_6''\\O\\OH\end{matrix}\right.$$

must be the rational formula of angelic acid.

Pyroterebic acid has no less than four possible formulæ, viz.:—

$$C_2\left\{\begin{matrix}H\\C_4H_8''\\O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}CH_3\\C_3H_6''\\O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}C_2H_5\\C_2H_4''\\O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}C_3H_7\\CH_2''\\O\\OH\end{matrix}\right.$$

Of these the second and fourth are excluded by reason of the products of decomposition which acids of such constitution would give in the test reaction. These products would be, for the second, two atoms of propionic acid, and for the fourth, valerianic and formic acids, whilst pyroterebic acid has been proved by Chautard* to yield butyric and acetic acids. The two remaining formulæ indicate acids both of which would give the same products of decomposition by potassium hydrate. The third represents ethyl-crotonic acid, with which pyroterebic acid cannot be identical, since the latter is liquid at − 20° C., whilst the former solidifies sharply at + 39·5° C.

Hence the rational formula of pyroterebic acid must be—

$$C_2\left\{\begin{matrix}H\\C_4H_8''\\O\\OH\end{matrix}\right.$$

The rational formula of oleic acid cannot be determined with the same degree of certainty, owing to the want of a synthesized acid with which to compare it. Of the sixteen possible formulæ for

* J. Pharm. [3], xxviii, 192.

this acid (the number of possible formulæ for any acid of this series being equal to the number of constituent atoms of carbon less two), fourteen are excluded by the nature of the products of decomposition by potassium hydrate, which acids of such a constitution would yield; leaving consequently only two which can express the internal architecture of oleic acid. These are—

$$C_2\begin{cases} H \\ C_{16}H''_{32} \\ O \\ OH \end{cases} \qquad C_2\begin{cases} C_{14}H_{29} \\ C_2H_4'' \\ O \\ OH \end{cases}$$

each of which expresses the composition of an acid, which, heated with potassium hydrate, would yield the same products as oleic acid, namely, acetic and palmitic acids. Further data are required to decide between these two formulæ, but from the circumstance that the remaining natural acids of this series, whose constitution is known, contain only one compound organic radical—a mode of construction which also seems to prevail in the natural acids of the lactic and acetic series—we believe that the first will eventually be found to be the rational formula of oleic acid.

The relations of the Acrylic to the Lactic Series of Acids.

The transformation of the lactic into the acrylic series of acids establishes a very simple relationship between the two series; in fact, it has been shown that the abstraction of the elements of one atom of water, from the basylous portion of an acid of the lactic family, converts that acid into the corresponding one of the acrylic family, thus—

$$C_2\begin{cases} C_2H_5 \\ C_2H_5 \\ OH \\ O \\ OH \end{cases} - H_2O = C_2\begin{cases} C_2H_5 \\ C_2H_4'' \\ O \\ OH \end{cases}$$

Diethoxalic acid. Ethyl-crotonic acid.

$$C_2\begin{cases} CH_3 \\ C_2H_5 \\ OH \\ O \\ OH \end{cases} - H_2O = C_2\begin{cases} CH_3 \\ C_2H_4'' \\ O \\ OH \end{cases}$$

Ethomethoxalic acid. Methyl-crotonic acid.

$$C_2\left\{\begin{matrix}CH_3\\CH_3\\OH\\\hline O\\OH\end{matrix}\right. \quad -- \quad H_2O \quad = \quad C_2\left\{\begin{matrix}CH_3\\CH_2''\\\hline O\\OH\end{matrix}\right.$$

Dimethoxalic acid. Methacrylic acid.

It will be seen from these equations, that, in the passage from the one series to the other, the hexatomic carbon type is preserved, since the abstraction of one atom of hydrogen, from one of the monatomic radicals of the original acid, converts the latter into a diatomic radical, thus filling up the atomicity vacated by the withdrawal of the atom of peroxide of hydrogen.

The relations of the Acrylic to the Acetic Series of Acids.

Simple as are the relations between the lactic and acrylic families, those connecting the acetic with the acrylic are even still more easily expressed. Rendered intelligible by the light which synthesis throws upon the constitution of the acrylic series, the action of potassium hydrate upon these latter acids proves, that they are derived from acids of the acetic family, by the substitution of a diatomic radical such as methylene, ethylene, &c., for two atoms of hydrogen. Thus acrylic acid is derived from acetic acid by the substitution of two atoms of hydrogen in the latter by one of methylene.

$$C_2\left\{\begin{matrix}H_3\\\hline O\\OH\end{matrix}\right. \qquad C_2\left\{\begin{matrix}H\\CH_2''\\\hline O\\OH\end{matrix}\right.$$

Acetic acid. Acrylic acid.

Although this transformation has not yet been realised, the inverse process is well known in the reaction of potassium hydrate upon acrylic acid, by which the latter is converted into acetic acid by the exchange of its methylene for two atoms of hydrogen. So far as the natural acids of the acrylic series have been studied, they all appear to derive from acetic acid, since they all yield this acid when heated with potassium hydrate. The artificial acids, on the other hand, all derive from acids in the acetic series higher than acetic acid. Thus methacrylic is methylene-propionic acid—

$$C_2\begin{cases}CH_3\\H_2\\\hline O\\OH\end{cases}$$

Propionic acid.

$$C_2\begin{cases}CH_3\\CH_2''\\\hline O\\OH\end{cases}$$

Methacrylic acid.

And in like manner, methyl and ethyl crotonic acids are respectively ethylene-propionic, and ethylene-butyric acids; thus—

$$C_2\begin{cases}CH_3\\H_2\\\hline O\\OH\end{cases}$$

Propionic acid.

$$C_2\begin{cases}CH_3\\C_2H_4''\\\hline O\\OH\end{cases}$$

Methyl-crotonic acid.

$$C_2\begin{cases}C_2H_5\\H_2\\\hline O\\OH\end{cases}$$

Butyric acid.

$$C_2\begin{cases}C_2H_5\\C_2H_4''\\\hline O\\OH\end{cases}$$

Ethyl-crotonic acid.

This extremely simple relation between the acetic and acrylic series, once pointed out, cannot fail to suggest appropriate reactions for the direct transformation of the former into the latter series. We may, in passing, suggest that the action of the haloid compounds of the diatomic radicals, upon the disodium compounds, recently described by us,* of the ethereal salts in the acetic series, could scarcely fail to effect the desired transformation. Thus dibromide of ethylene and ethylic di-sodacetate would probably yield ethylic crotonate.

$$C_2\begin{cases}H\\Na_2\\\hline O\\OC_2H_5\end{cases} + C_2H_4''Br_2 = C_2\begin{cases}H\\C_2H_4''\\\hline O\\OC_2H_5\end{cases} + 2NaBr$$

Ethylic disodacetate. Ethylic crotonate.

The nature of the change, by which acetic acid is converted into the acids of the acrylic series, suggests the existence of another family of acids, derived from acetic acid by the substitution of a triatomic radical for three atoms of hydrogen in the basylous part of acetic acid. The first acid of this series would be formyl-acetic acid with the formula—

$$C_2\begin{cases}CH'''\\\hline O\\OH\end{cases}$$

* Proceed. Roy. Soc., vol. xiv, p. 198.

The Extension of the Acrylic form of Acids to the Benzoic Series.

The close relations known to exist between the benzoic and acetic series of acids, scarcely leave a doubt that there must be a family of acids, holding the same position with regard to the benzoic series as the acrylic maintains by the side of the acetic; in fact, the probable existence of such acids has already been pointed out by Chiozza,* who names cinnamic acid as one of the series, and proves that this acid, when treated with potassium hydrate, yields benzoic and acetic acids. This reaction, however, still leaves it undecided whether cinnamic acid is toluylene-acetic acid or ethylene-benzoic acid.

$$C_2\begin{cases}H\\ C_7H_6''\\ O\\ OH\end{cases} \qquad C_2\begin{cases}C_5H_3\\ C_2H_4''\\ O\\ OH\end{cases}$$

Toluylene-acetic acid. Ethylene-benzoic acid.

An acid possessing either of these formulæ would yield acetic and benzoic acids on treatment with potassium hydrate. Any method of general application for the production of the members of the acrylic family from acetic acid would, doubtless, when applied to benzoic acid, furnish an extensive benzacrylic series by the introduction of the various olefines into benzoic acid.

Constitution of the Allylic Series.

The obvious analogy that exists between the relations of acrylic acid and allylic alcohol on the one hand, and of acetic acid and vinic alcohol on the other, permits us to draw certain conclusions regarding the constitution of allylic alcohol, from what we now know of that of acrylic acid. If, in accordance with the notation adopted in this paper, we formulate vinic alcohol and acetic acid thus—

$$C_2\begin{cases}H_3\\ H_2\\ OH\end{cases} \qquad C_2\begin{cases}H_3\\ O\\ OH\end{cases}$$

Alcohol. Acetic acid.

it follows that allylic alcohol and acrylic acid ought to be expressed as follows:—

* Ann. Ch. et de Phys., xxxix, 435.

$$C_2\begin{cases} H \\ CH_2'' \\ \overline{H_2} \\ OH \end{cases} \qquad C_2\begin{cases} H \\ CH_2'' \\ \overline{O} \\ OH \end{cases}$$

Allylic alcohol. Acrylic acid.

Such a generalization must, however, be received with great caution, until the habits of allylic compounds, and especially their relation to the triatomic compounds of allyl, have been further investigated.

In conclusion, the extension of this reaction to the ethers of other acids, in which the so-called atomicity is greater than the basicity, such as malic and tartaric acids, can scarcely fail to throw light upon the constitution of these acids, and we propose further to prosecute our inquiries in this direction.

We append a table of the acids of the acrylic series already known, giving the rational formulæ, where these have been ascertained :—

Acids of the Acrylic Series.

Name.	Formula.
Acrylic acid	$C_2\begin{cases} H \\ CH_2'' \\ \overline{O} \\ OH \end{cases}$
Methacrylic acid	$C_2\begin{cases} CH_3 \\ CH_2'' \\ \overline{O} \\ OH \end{cases}$
Crotonic acid	$C_2\begin{cases} H \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases}$
Methyl-crotonic acid	$C_2\begin{cases} CH_3 \\ C_2H_4'' \\ \overline{O} \\ OH \end{cases}$
Angelic acid	$C_2\begin{cases} H \\ C_3H_6'' \\ \overline{O} \\ OH \end{cases}$

Ethyl-crotonic acid..... $C_2\left\{\begin{matrix}C_2H_5\\C_2H_4''\\O\\OH\end{matrix}\right.$

Pyroterebic acid..... $C_2\left\{\begin{matrix}H\\C_4H_8''\\O\\OH\end{matrix}\right.$

Damaluric acid ..... $C_7H_{12}O_2$

Moringic acid..... $C_{15}H_{28}O_2$

Physetoleic acid ..... $C_{16}H_{30}O_2$

Oleic acid ..... $C_2\left\{\begin{matrix}H\\C_{16}H_{32}''\\O\\OH\end{matrix}\right.$?

Doeglic acid ..... $C_{19}H_{36}O_2$

Erucic acid..... $C_{22}H_{42}O_2$.

XXVI.—*On Lecture Illustrations.*

By A. W. Hofmann.

[A Discourse delivered to the Members of the Chemical Society on February 2, 1865.]

The introduction into modern chemistry of the idea of structural types, and the prominence given thereby to volumetric considerations, involve the necessity of modifying, to a certain extent, our present style of experimental illustrations. This necessity, I believe, has been felt by many teachers who have endeavoured to reflect the present aspect of chemistry in their lectures. In these endeavours many new and interesting experiments must have been devised already; and if an interchange of the valuable information thus acquired could be effected, a large expenditure of time and labour would be saved to those engaged in teaching chemistry. The Chemical Society, comprising as it does a great many professors of our science, appears to be an appropriate centre

to attract this floating knowledge for condensation and distribution. It is in the conception of this mutual benefit which we might derive from communications of this kind, that I venture to submit to the Society an account of some of the volumetrical experiments on the composition of the typical hydrogen compounds, with the study of which, during the last few years, I have been in the habit of opening my course of lectures on experimental chemistry.

Hydrochloric Acid.

The usual method of illustrating the composition of hydrochloric acid, recommended in Manuals on Experimental Chemistry, consists in introducing a small ball of sodium into a volume of the gas, confined over mercury. Since the metal has to be heated, the upper part of the tube is bent (*cloche courbe*). It need scarcely be mentioned that a vessel of this form is very little appropriate for comparing the volume of the hydrochloric gas with the volume of the hydrogen gas evolved by the action of sodium; hence the necessity of measuring the gas in a graduated tube, of transferring it to the *cloche courbe*, and of re-transferring it to the graduated vessel, after the action has taken place. The experiment thus becomes tedious, difficult, and inaccurate. Again, how is it possible to introduce the metallic sodium into the gas without its surface having become oxidized? Not to speak of the rapidity with which the metal is amalgamated during its passage through the mercury.

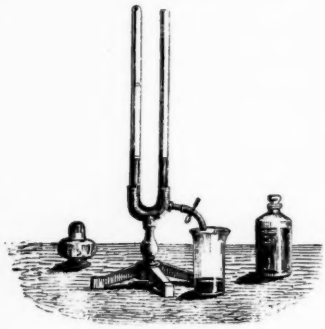
By adopting the following mode of proceeding these difficulties are in a great measure obviated.

A U-shaped glass tube, about 50 centimetres long by 1·5 in diameter, having one sealed and one open limb, is fixed upon a convenient stand. Just above the bend of the tube, the open limb has a small outlet tube (blown on at the lamp), and to this is affixed a piece of caoutchouc tubing, with an elastic wire nipper (*nipper-tap*) attached, or provided with a screw (*screw-tap*), by the action of which the caoutchouc tube is pinched close, but can be readily opened at pleasure.

This apparatus has to be filled with an appropriate volume of the gas to be examined. For this purpose the U-tube is first filled with mercury, and then the nipper-tap is set open, so as to afford a gradual exit to the metal in the open limb. The delivery-tube of a gas-generating apparatus is then passed down the open limb to the bend of the tube, in such a manner

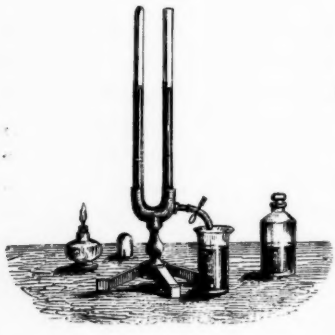
that the gas bubbles up through the mercury into the sealed limb, from which, of course, the metal escapes as the gas enters, volume for volume. An appropriate quantity of dry hydrochloric acid gas having been thus introduced, the nipper-tap is closed, and mercury is poured into the apparatus, until it stands at the same level in both limbs. The space occupied in the tube by the gas is then marked in any convenient way; preferably by a caoutchouc ring slipped over the tube (Fig. 1).*

Fig. 1.



That portion of the open limb which is unoccupied by mercury is then filled with sodium-amalgam, and the orifice of the tube is closed, either by the thumb or, more conveniently, by a glass-stopper. The gas may now, by inclining the tube adroitly, be easily transferred from the sealed to the stoppered limb; traversing of course, in its passage, the column of sodium-amalgam, and being thereby decomposed. To insure complete decomposition, the apparatus should be once or twice shaken, so as to bring every portion of the gas into thorough contact with the amalgam; after which, by reversing the previous inclination of the tube, the gas may be re-transferred to the sealed limb of the apparatus. On removing the stopper or thumb from the mouth of the open limb, the mercury falls a little therein, and may be further lowered by opening the nipper-tap. As soon as the mercury stands at a uniform level in the two limbs, the gas is found reduced to exactly half its original volume (Fig. 2). The residuary gas is readily recognised as hydrogen, by transferring it to the open limb; or, the closed limb may be provided with a

Fig. 2.



* The illustrations given in this Lecture are taken from a little work, shortly to be published, entitled, *Introduction to Modern Chemistry, Experimental and Theoretic: Lectures delivered in the Royal College of Chemistry, London.*

glass stop-cock (see Fig. 11), and the hydrogen expelled by pouring mercury into the open limb. In either way the gas is found to be inflammable, and to burn with the pale flame of hydrogen gas.

This experiment shows us that a given bulk of hydrochloric acid contains half that bulk of hydrogen. It only remains, therefore, to determine with what proportion, by volume, of chlorine, this bulk of hydrogen is combined in hydrochloric acid.

This we learn from a second experiment. We submit hydrochloric acid to electrolysis in any convenient apparatus which permits collecting the gases evolved during the process. At starting, the chlorine is almost entirely absorbed by solution in the surrounding liquid; nor is it till this is saturated that the chlorine begins to be manifested in a stream of bubbles, like those which, from the first, mark the escape of hydrogen at the opposite pole. At this stage of the process, the delivery-tube of the apparatus is attached, by means of a caoutchouc connecter, to a glass tube, about 40 or 50 centimetres long by 1·5 centimetre in diameter, drawn out, before the lamp, to a fine point at each end. This tube is thus filled with the mixture of hydrogen and chlorine evolved by the electrolysis of hydrochloric acid. In order to expel every trace of air, it is necessary that the mixed gases should be suffered to traverse the tube for a considerable time. To prevent the chlorine escaping into the air, the free end of the tube is connected with the lower part of an upright cylinder containing coke, moistened with an alkaline liquid capable of absorbing the chlorine. After the lapse of one or two hours the operation may be considered complete. The tube being now detached, its fine-drawn ends are immediately sealed.

The tube having been sealed at each end, its gaseous contents have next to be examined. For this purpose, it is requisite to bring the mixed gases into contact with a liquid capable of absorbing the chlorine, but not the hydrogen. Water, of course, answers this purpose, but a little soda may be conveniently mixed with it to increase its absorptive power. Again, the addition of a vegetal colour—of an infusion of logwood, for instance—to tint the soda-solution employed, is useful as a means of evincing the presence of chlorine by exhibiting its bleaching action on the colour, so soon as it comes into contact therewith. By plunging the sealed finely-drawn extremity of the tube into a solution so prepared, and then

breaking it off, the desired contact is effected, absorption begins, and the liquid is seen slowly rising into the tube to occupy the space vacated by the absorbed chlorine. This absorption goes on very slowly, however, because of the extreme minuteness of the surface of fluid exposed to the gas in the finely-drawn tube represented by the broken extremity. A great acceleration would evidently be obtained if the surface of contact could be extended; if, for example, we could wet the whole interior surface of the tube with the absorptive liquor.

Fig. 3.

A very simple contrivance (Fig. 3) accomplishes this object.

It consists of a caoutchouc connecter tightly fitted to the end of the tube, so as to cover and enclose its fine-drawn sealed neck. This connecter is provided with a small glass funnel, through which it can be filled with a tinted solution of soda; and has also a stop-cock, by which, when so filled, it can be closed. These arrangements being made, the fine-drawn neck is immersed in the solution, so that, on breaking it (Fig. 4), which the flexibility of the connecter allows to be easily done, the solution finds its way through the orifice into the interior of the apparatus.

Fig 4.

By suitably inclining this, the solution may be caused to extend in a film over its interior, so as to expose a widely-spread surface to the gaseous mixture. The absorption of the chlorine is thus made to proceed with greatly increased rapidity, as is evinced by the speedy ascent of a small volume of the liquid into the wide part or body of the tube. This accomplished, that end of the tube which is armed with the tap-funnel and its flexible connecter, may be plunged under water, the connecter withdrawn, and the experiment continued in the ordinary way, by allowing the absorption to proceed, and the column of liquid to ascend in the tube till all the chlorine is absorbed. This is known to have taken place by the liquid ceasing to rise in the tube.

The tube is now to be more deeply immersed in the water (the receptacle for which should be a tall glass cylinder, to facilitate this part of the manipulation), until the level of the liquid within and without the tube is brought into coincidence. It is then found that the tube is just half-filled with liquid—in other words, that just half its gaseous contents have been absorbed. That the absorbed gas is chlorine is readily proved by the bleaching effect exerted by it on the logwood solution.

The nature of the residuary gas is as readily demonstrated by immersing the tube more deeply in the surrounding liquid, then breaking off its upper finely-drawn point and applying to the jet of gas, thus forced out by water pressure, a lighted taper, when it immediately takes fire, and burns with the characteristic pale flame of hydrogen.

These phenomena furnish a simple and satisfactory reply to the question left unanswered by our previous experiment.

The action of sodium upon hydrochloric acid has taught us that 2 volumes of hydrochloric acid contain 1 volume of hydrogen; the electrolysis of hydrochloric acid proves that, to form hydrochloric acid, 1 volume of hydrogen combines with 1 volume of chlorine.

The two experiments, taken together, supply us with the exact points of information which our previous investigation of hydrochloric acid left deficient; so that, summing up our previous and present results, we now possess a complete and irrefragable demonstration, first, that hydrochloric acid is *composed* of hydrogen and chlorine; secondly, that these two elements are its *sole* constituents; thirdly, that they are united in *equal volumes* to form it; and, lastly, that, in so uniting, they undergo *no condensation*, but produce a volume of compound gas, equal to the sum of the volumes of its elementary constituents.

This last-mentioned fact—the union of hydrogen and chlorine without contraction or expansion—may be illustrated by another, and an equally conclusive, experiment. While the electrolytic apparatus, used in the experiment just made, is still evolving hydrogen and chlorine in the proportion in which the two gases exist in hydrochloric acid, we may replace the wide glass tube, previously used, by another tube of equal length, but of stouter glass, and of smaller bore, half a centimetre being a convenient diameter. The two ends of this tube are, like those of the tube used in the previous experiment, drawn out into very fine necks.

As soon as the tube is thoroughly purged of air, and exclusively filled with the gaseous constituents of hydrochloric acid, its fine necks are sealed by the blow-pipe jet, and its contents are exposed to the action of light for the purpose of inducing the combination of the mixed gases.

This effect, as is well known, may be obtained either by natural or artificial light. The direct rays of the sun produce instantaneous combination. But as such rays are not at our command in all seasons and at all places, as, for instance, during the earlier weeks of a London winter, it is necessary to employ an artificial light sufficiently intense to bring about the same effect. Such a light is that of the blue flame produced by the combustion of bisulphide of carbon in nitric oxide. The manipulation for generating this light is very simple.

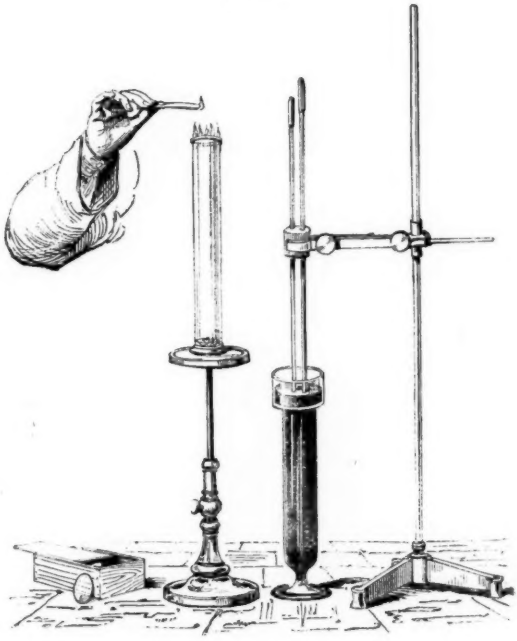
For this purpose some 8 or 10 cubic centimetres of bisulphide of carbon are introduced into a tall glass cylinder filled with nitric oxide gas. This is most conveniently accomplished by means of a very thin bulb of glass, blown to the required size, filled with the bisulphide, and then sealed at the lamp. The glass cover of the vessel, already filled with nitric oxide gas, is drawn aside, the bulb dropped in, and the cover quickly replaced. Contact of atmospheric air is thus almost entirely obviated. The vessel is then shaken, so as to break the glass bulb, and the desired mixture of gas and vapour is at once obtained. A match is now applied to the opened mouth of the cylinder, when the mixture within takes fire, and burns with a brilliant, intensely blue flame, which descends into the vessel. The radiance of this light instantaneously induces the combination of hydrogen and chlorine; the effect being indicated by a flash of light, accompanied by a slight clicking sound, and followed immediately by the disappearance of the greenish colour of the mixture.

The figure (5) shows the disposition of the apparatus. To the left is the glass cylinder in which the light is generated; to the right are placed the mixed gases to be acted on, two tubes instead of one being filled therewith and employed in the experiment, to afford a double chance of success—since the combination occasionally fails from causes not yet perfectly ascertained.

For the purpose of examining the product, one point of the tube is broken under mercury; when the first indication is immediately obtained. It is observed that neither does gas escape from, nor mercury penetrate into, the tube; from which it is clear that

the combination of the gases has taken place without either contraction or expansion of their volume.

Fig. 5.



The next indication is obtained by pouring water on the mercury, and raising the tube so that its orifice, instead of plunging into mercury, may open into water. The water no sooner comes into contact with the gas than this latter is dissolved; and so rapid is the absorption that the water rising in the tube, fills it almost instantaneously. We thus obtain an additional experimental proof that hydrochloric acid is formed by the union of hydrogen and chlorine gases, in equal volumes, without condensation.

In performing this experiment, whether sunlight or the light of bisulphide of carbon be employed, some manipulatory precautions are necessary to shield the operator from possible injury by the explosion of the tubes. The experimentalist should not omit to protect himself by a screen, for which purpose a sheet of stout plate-glass may be conveniently employed. Thus, even should the tube explode, the dangerous scattering of its fragments is prevented. It is, however, only rarely that the body of the tube

is shattered; in most cases the fracture is confined to one or other of the sealed points. To avoid the loss of the experiment by an accident of this kind, the upper point of the tube may be strengthened by imbedding it in sealing-wax, which may be most conveniently applied by fusing a little in a small piece of glass tube sealed at one end, and plunging the point to be protected into the fused mass, which is then allowed to cool and harden. As for the lower point, escape of gas from this, in case of rupture, is readily obviated by keeping it immersed in a trough-cylinder filled with mercury.

Water.

The ratio in which hydrogen and oxygen are associated in water is, of course, most conveniently established by the electrolysis of this compound.

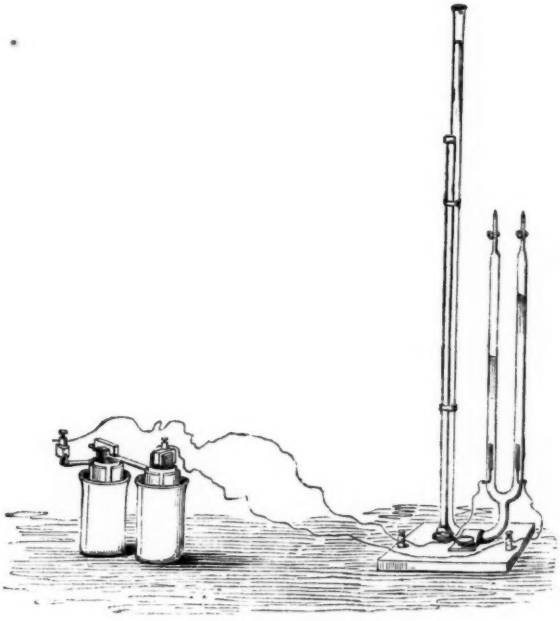
Among the numerous contrivances used for decomposing water, an apparatus constructed some time ago by Professor Buff, of Giessen, deserves to be especially mentioned. The two tubes for the collection of the gaseous constituents of the water are provided with brass stop-cocks, and plunged into a deep cylinder filled with water. As the gases are evolved, the water-level in the tubes is depressed below the level in the cylinder, and on opening the stop-cocks, the gases escaping under the pressure of the short water column may be conveniently examined.

Fig. 6 shows an improved form of this apparatus. Instead of the two stop-cock tubes separately inverted in a basin, as just described, I have adopted a three-branched tube, with one long and two short limbs. The long limb acts as a water-reservoir, instead of the basin; the two short limbs, which are fitted with stop-cocks, or nipper-taps, above, and which communicate freely with the long limb below, contain, intermediately, each a platinum electrode. When this apparatus is used, the water in the short limbs is forced downward out of these, so as to rise in the long limb, forming a column, the weight of which serves, afterwards, to expel the gas from each short limb through the corresponding stop-cock, when this is opened for the purpose of testing the nature of the gas obtained.

It now remains only to be demonstrated that two volumes of hydrogen and one volume of oxygen, when combined, yield two volumes of water-gas. This fact, familiar to us from the earliest stage of our chemical education, is, strangely enough, scarcely

ever demonstrated by experiment in our lectures. As to myself, I have only lately, since the volumetric conception of matter has

Fig. 6.



acquired such predominant importance, commenced performing this experiment.

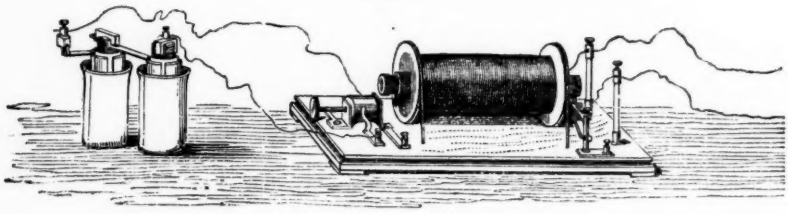
The object to be achieved is the comparison of the volume of the elementary water-constituents with that of the water formed, at a temperature high enough to maintain the latter in a purely gaseous condition.

The experiment is made in a U-tube similar to that used in analysing hydrochloric acid. The closed limb of the tube is, however, fitted, at a point near its sealed extremity, with two platinum wires, for the purpose of passing the electric spark; this operation I now invariably perform by means of the induction-coil.

A glance at Fig. 7 shows how this apparatus is employed. Into the sealed limb of the apparatus, which is filled with mercury, we admit a column, about 25 or 30 centimetres high, of a mixture of hydrogen and oxygen in the proportions in which they form water. This mixture may of course be obtained by adding two volumes of hydrogen to one of oxygen; it is, however, prepared much more

readily in due volumetric proportion, and in a state of perfect purity, by the electrolysis of water. The gas-filled limb of the apparatus is surrounded by a high glass cylinder, the lower mouth of which is fastened around it by means of a perforated cork, whilst its upper mouth (likewise closed by a cork) rises about five centimetres above the sealed extremity. The annular space thus formed communicates, at its upper end, by means of a bent glass tube and a perforated cork, with a flask which contains a liquid

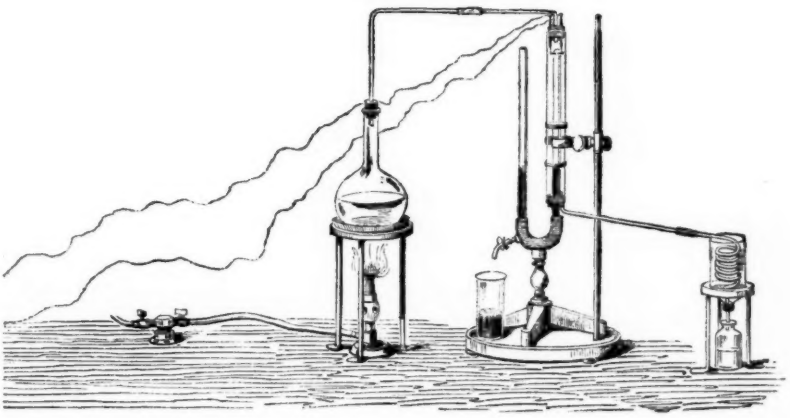
Fig. 7.



having a boiling point considerably above that of water; amylic alcohol, which boils at 132° C., is well adapted for the experiment. On protracted ebullition, the vapour descends from the flask into the annular space, which rapidly acquires a uniform temperature of 132°. To prevent the vapours from escaping into the atmosphere, the lower extremity of the glass cylinder is connected with an appropriate vapour-condenser, such as a glass coil kept cool by water. Under the influence of heat, the column of mixed hydrogen and oxygen in the tube expands. The level of the mercury in both limbs of the apparatus having been adjusted, the height of the gas columns is now marked by any suitable means; preferably by slipping a caoutchouc ring over the outer glass cylinder. A little more mercury is then poured into the open limb, which is, lastly, closed by a well-fitting cork. Between this cork and the mercury intervenes a column of air, some eight or ten centimetres in length, and capable of yielding to pressure, like a spring. It now only remains to inflame the gaseous mixture by causing the current of the induction-coil to leap, in the form of a spark, between the platinum points. The gases combine with an explosion, which is, however, much mitigated in violence by the elastic action of the above-mentioned air column. At the high temperature employed (132°) the water formed retains the gaseous condition. On removing the cork, and allowing the mercury to flow

through the nipper-tap, until it is level in both limbs, it becomes obvious that the original measure of mixed gases is diminished

Fig. 7.



by one-third; the residuary two-thirds are water-gas, which condenses into liquid water so soon as the apparatus is allowed to cool.

Thus, therefore, it stands experimentally demonstrated, first, that hydrogen and oxygen undergo condensation in combining to form water; and, secondly, that the volume of the water-gas produced holds an extremely simple ratio to the volume of its constituent gases, two volumes of hydrogen and one volume of oxygen condensing, by their union, into two volumes of water-gas.

Ammonia.

The method of ascertaining the volume-ratio in which hydrogen and nitrogen combine to form ammonia is less simple than that which suffices for the corresponding study of hydrochloric acid and water.

For this purpose we avail ourselves of chlorine, which enables us to withdraw the hydrogen from ammonia, and set free the nitrogen; the experiment has, of course, to be made under circumstances which permit the determination with accuracy of the volume of nitrogen thus separated from a known quantity of ammonia.

A glass tube for holding chlorine, and a globe for receiving solution of ammonia, and admitting it, drop by drop, to the

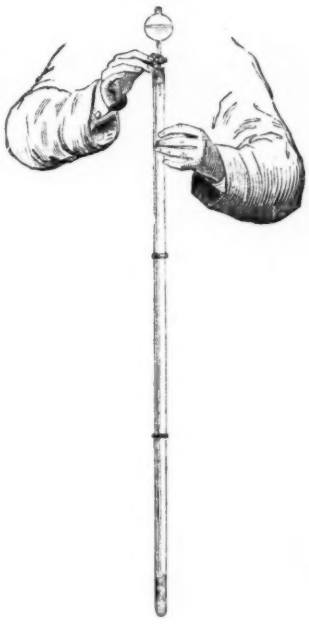
chlorine, constitute the requisite apparatus. The glass tube is from 1 to 1·5 metre long, sealed at one end, open at the other, and marked off by elastic caoutchouc rings, slipped over it and clipping it firmly, into three equal divisions. The globe (Fig. 8) has a stoppered aperture above, and a dropping tube drawn out to a narrow orifice below. This tube is fitted with a stop-cock, and passes through a perforated cork, by means of which it can be tightly fixed into the open mouth of the chlorine-tube.

Fig. 8.

The apparatus is thus employed. The long chlorine tube having been filled with cold water and inverted over a pneumatic trough, with its mouth immersed below the water-level, is filled with chlorine gas in the usual way. When full, it is still allowed to stand for about fifteen minutes over the chlorine-delivery-tube, that its interior surface may be quite freed from the chlorine-saturated water that else would remain adherent thereto. The globe, meanwhile, is filled with a strong solution of ammonia, and its stop-cock is turned so that its dropping-tube also may be filled to its very tip with this solution. The cock is then again closed and the globe stoppered; after which it is ready for connection with the chlorine-tube. To effect this connection without admission of air into the chlorine-tube, requires some little care and dexterity. The globe has to be immersed in the pneumatic trough, with its dropping-tube upwards, and in this position to be brought beneath the mouth of the chlorine-tube, into which the globe-tube is inserted, and fixed firmly by means of the cork which it carries. In effecting this junction, great care must be taken not to introduce any water from the trough into the chlorine-tube. This tube, with its ammonia-globe joined to it, may now be removed from the trough, and supported in a vertical position, with the globe surmounting it. A single drop of the ammonia-solution is now suffered to fall from the globe into the chlorine-tube, the stop-cock being opened for a moment for this purpose (Fig. 9). The entrance of this drop into the atmosphere of chlorine is marked by a small, lambent, yellowish-green flame at the drawn-out point of the dropping-tube. Drop by drop, at intervals of a few seconds, the ammonia-solution is allowed to fall into the chlorine-tube, the ammonia of each drop being, at the instant of its contact with the chlorine, converted, with a flash of light and the formation of a dense white cloud, into hydrochloric acid and nitrogen. The

addition of ammonia must be continued till the whole of the chlorine present is supplied with hydrogen at the expense of ammonia. To insure this, the ammoniacal solution is added in excess, a column of three or four centimetres being abundantly sufficient. After a few seconds the interior of the tube is lined with a deposit of chloride of ammonium; this being soluble, is readily washed down and dissolved by agitating the liquid in the tube, which now contains the whole of the nitrogen separated, except a little which remains dissolved in the liquid. This small quantity of dissolved nitrogen is easily expelled from the liquid by heat.

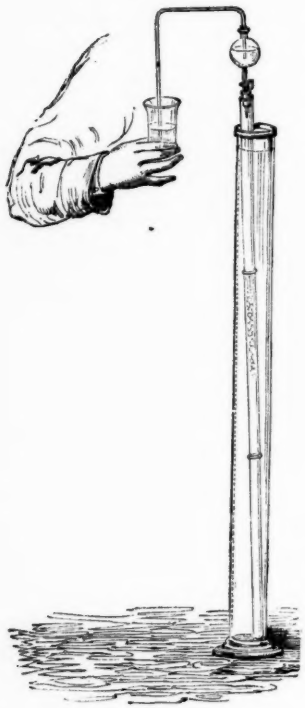
Fig. 9.



We are now sure of two points; viz., that the whole of the chlorine has been converted into hydrochloric acid at the expense of the ammonia; and, secondly, that we possess within our tube the whole of the nitrogen thus set free. It becomes our next object to withdraw the excess of ammonia. For this purpose dilute sulphuric acid, which fixes the ammonia, is introduced by means of the globe previously employed to admit ammonia. The nitrogen being thus freed from all intermixed gaseous bodies, has only now to be brought to mean atmospheric temperature and pressure in order to be ready for measurement.

The temperature, which had been raised by the application of heat to the liquid, to expel the dissolved nitrogen therefrom, is readily reduced by plunging the tube into cold water. Water must now be admitted into the tube until the pressure inside and outside is brought to a state of equilibrium. This is effected by means of a bent syphon-tube plunging into a cup of water and fixed by a cork into the globe (Fig. 10). As soon as water ceases to flow through the syphon into the tube, all the requisite conditions are fulfilled for obtaining an exact knowledge of the volume of nitrogen; and this, on inspection, is found exactly to fill one of the three divisions marked off on our tube at the outset.

FIG. 10.

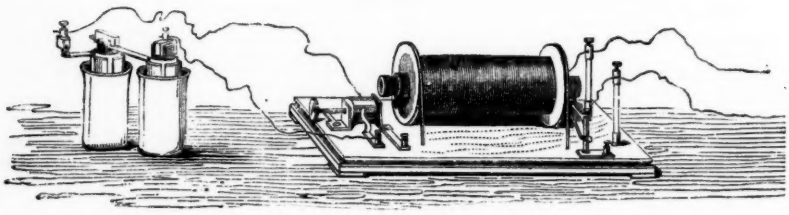


Now, bearing in mind that we started with the three divisions full of chlorine, and that we have saturated this chlorine with hydrogen supplied by the ammonia; bearing in mind, moreover, that hydrogen combines with chlorine, bulk for bulk; it is evident that the one measure of nitrogen which remains in the tube has resulted from the decomposition of a quantity of ammonia containing three measures of hydrogen. It is, therefore, clearly proved by this experiment that ammonia is formed by the union of three volumes of hydrogen with one volume of nitrogen.

Thus much determined, it remains to ascertain the condensation undergone by these elements in combining to form ammonia.

The direct synthesis of ammonia having never yet been accomplished, we must fall back upon analysis to furnish us with this demonstration. We must split up a measured quantity of ammonia into its constituents, and compare the space occupied by the ammonia before treatment with the space filled by its separated constituents. This we are enabled to do very easily, by availing ourselves of the tendency of ammonia to break up into its elements under the influence of a moderate heat. The spark-stream supplied by the electric current in traversing the induction-

FIG. 11.



coil may be conveniently used as a source of heat. Among the many forms of apparatus which suggest themselves for this purpose, I find the following disposition (Fig. 11) most appropriate.

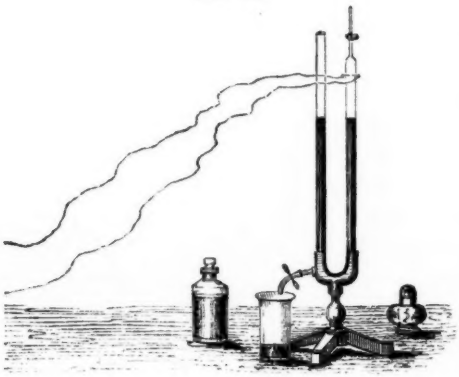
The sealed limb of a U-tube is filled about one-third full with dry ammonia, over mercury, and the height of the column of gas is accurately measured, care having been taken, as usual, to bring the mercury in each limb of the tube to a uniform level. The spark-stream is now set flowing between the platinum points, and the volume of the gas on which it acts is immediately observed to increase. This dilatation continues for some five or ten minutes (according to the quantity of ammonia under treatment); and, when it ceases, the level of the mercury (disturbed, of course, by the expansion of the gas) is re-adjusted to perfect uniformity in both limbs of the tube, when it is immediately perceived that the original volume of gas has become doubled. If a little of the gas (previously so pungent) be allowed to escape from the tube, by a stop-cock provided for that purpose, it is found to have become inodorous, while the presence of hydrogen is indicated by its inflammation on the approach of a light.

This experiment proves that hydrogen and nitrogen, as combined in ammonia, occupy only half the space they fill in their free state; or, in other words, that 4 volumes of the mixed gaseous constituents of ammonia, composed, as we have already ascertained of 3 volumes of hydrogen and 1 volume of nitrogen, condense, during their combination, to form 2 volumes of ammonia.

Marsh-gas.

The only fact connected with the history of this compound which admits of convenient illustration, is the existence in a given volume of marsh-gas of its double volume of hydrogen. This demonstration is furnished in very close approximation by the method which served us in the case of ammonia, viz., by splitting it up into its constituents under the influence of heat. This experiment we perform, as

Fig. 11.



before, in a U-tube fitted up with spark wires, and as source of heat we again employ the spark-current of the induction-coil. On transmitting the current, the marsh-gas expands, and after the lapse of a few minutes, a light deposit of carbon is formed in the vicinity of the platinum wires. The decomposition, energetic at the commencement of the experiment, proceeds more slowly as the gas dilates; but if, after fifteen or twenty minutes, the mercury be allowed to run out from the nipper-tap till it has become level in the two limbs of the U-tube, it is found that the original gas-volume has very nearly doubled. This result having been attained, the continued transmission of the spark-current produces no further increase in the volume of the gas, which is now found to consist of hydrogen.

This experiment presents greater difficulty of manipulation than either of the preceding. The spark-current, when transmitted through marsh-gas, is not unfrequently interrupted by the formation of a conducting-bridge of carbon between the platinum-points. This bridge may, however, be broken by agitating the mercury in the tube until it touches the platinum wires; or its formation may be prevented by reversing the direction of the current from time to time.

With these precautions, the experiment affords very closely approximative, though not perfectly exact, results, a slight error arising from a minute proportion of marsh-gas suffering a different decomposition, so that the volume of the hydrogen obtained is never quite double that of the marsh-gas submitted to the treatment. Nevertheless, the experiment, even in this imperfect form, unequivocally demonstrates that marsh-gas contains twice its volume of hydrogen.

I have made numerous experiments with the view of finding a shorter, simpler, and, more especially, a more accurate method of exhibiting the volume of hydrogen which is present in a given bulk of marsh-gas, but hitherto without result. Eudiometrically, of course, the composition of marsh-gas is given in a single most elegant experiment, which acquires additional charm when performed at a temperature higher than that of boiling water in an apparatus similar to the one employed in determining the ratio of the volume of water-gas to that of its constituents. But at the stage of the course at which I am in the habit of examining the nature of marsh-gas, an experiment of this description is unintelligible to the student, and hence simply out of the question.

XXVII.—*On the Action of Nascent Hydrogen on Azodinaphthyldiamine.*

By W. H. Perkin.

The metamorphoses which bodies undergo, when subjected to the influence of nascent hydrogen, have been made the subject of numerous investigations, the results of which have shown it to possess various functions: for at one time we find it converting nitro-compounds into ammonia, at another replacing the halogens, and sometimes uniting directly with bodies, as in the conversion of maleic and fumaric acids into succinic acid; while the results of this investigation show that hydrogen may also act in an entirely different manner, and may cause a total breaking up of the body submitted to its influence.

The fact that azodinaphthyldiamine is decolorized, when submitted to the influence of nascent hydrogen, was mentioned in a paper by Professor Church and myself, published some time back in the Society's Journal. Since then I have fully investigated the products of this reaction. The following are my results:—

When a saturated alcoholic solution of azodinaphthyldiamine is mixed with concentrated hydrochloric acid, it acquires a brilliant violet colour.* This solution, on being digested with granulated tin, gradually changes to a pale buff tint. The solution is then decanted from the undissolved tin, and the excess of alcohol distilled off in a water-bath. The residue, after dilution with water, is treated with sulphuretted hydrogen until sulphide of tin ceases to be thrown down. It is then filtered, and the filtrate evaporated to dryness. This operation should be performed as quickly as possible, otherwise a considerable amount of product will be lost from oxidation. The dried residue is purified by solution in a small quantity of boiling water, and after filtration strong hydrochloric acid is added to facilitate its crystallization. On standing for 24 hours it will become nearly solid from the deposition of crystals.

This crystallized product is to be thrown on a filter to drain, and must then be washed once or twice with dilute hydrochloric acid, in which it is nearly insoluble, and then dried. The results of the examination of the mother-liquors from this product will be found further on.

* Owing to the formation of its hydrochlorate, $C_{20}H_{15}N_3,2HCl$.

The dried product I have found to consist of the hydrochlorates of two bases, one of which is naphthylamine, and the other a new base isomeric with naphthenediamine (azonaphthylamine*). The hydrochlorate of this new base is separated from the hydrochlorate of naphthylamine by digestion in absolute alcohol, in which it is very difficultly soluble. Nevertheless, the naphthylamine salt causes a considerable quantity of this new product to be taken up by the alcohol, and it is found worth while to evaporate the alcoholic solutions obtained in its purification to dryness, and to re-extract first with cold and then with boiling alcohol, as by this means an additional amount of substance may be obtained.

When I first made these experiments I had some doubts as to whether the hydrochlorate which dissolves in alcohol was really a salt of naphthylamine, and although, on distilling it with an alkali, I obtained a base having all its properties, yet it appeared to me that such a result might be owing to a decomposition; but, on testing it with nitrite of potassium, it yielded the characteristic scarlet reaction due to the formation of azodinaphthyldiamine, and results obtained in the examination of its platinum salt left no room for doubt on this point. A portion of this product distilled with potash, and re-converted into the hydrochlorate, was burnt with chromate of lead, and gave the following numbers:—

·3334 of substance gave
·8145 of CO_2, and
·1750 of H_2O,

which give percentages agreeing closely to those required by theory.

		Theory.		Experiment.
C_{10}	=	120	66·85	66·62
H_{10}	=	10	5·57	5·83
N	=	14	7·80	—
Cl	=	35·5	19·78	—
		179·5	100·00	

The crude hydrochlorate, left after the removal of the excess of

* The name "Naphthalene" having now been applied to the hydrocarbon formerly called "naphthaline," a new one is required for the radical $C_{10}H_6$. I therefore propose to call it *naphthene*. The base $\left.\begin{matrix}C_{10}H_6''\\H_4\end{matrix}\right\}N_2$ will consequently be called *naphthenediamine*.

the naphthylamine-salt by means of absolute alcohol, requires repeated digestion with fresh quantities of that solvent, as it still contains hydrochlorate of naphthylamine, which adheres to it with remarkable pertinacity. It is then to be dried and crystallized from water. From this salt the new base, which I propose to call *naphthyldiamine*, may be obtained.

Naphthyldiamine. This base is remarkable for the rapidity with which it oxidizes; in fact, so rapid is the change that takes place when it is exposed to the influence of the atmosphere, that if one of its salts be treated with an alkali so as to liberate the base, it will become converted in a few minutes into a dark-green, dirty mass. Nevertheless, it is a beautiful crystalline substance, and, if to a saturated solution of its hydrochlorate, potash or ammonia be added, it at first becomes turbid, but in a few minutes the vessel in which the experiment is performed is filled with beautiful glistening scales of the base.

Naphthyldiamine, when distilled in a retort blackens before it reaches the receiver; it may however be distilled in a current of hydrogen with but little change. A quantity was prepared by distilling the sulphate with potash in an atmosphere of hydrogen, and then rectified also in a current of hydrogen, the first portions being kept for analysis. In this manner it was obtained as a pale yellow oil, which immediately solidified into a crystalline mass on cooling; doubtless if absolutely pure, it would be colourless. Its odour is somewhat similar to that of naphthylamine. A combustion of this product gave the following numbers :—

·2527 of substance gave
·7094 of CO_2, and
·1560 of H_2O,

which give percentages agreeing with the formula

$$C_{10}H_{10}N_2,$$

as the following comparisons will show :—

	Theory.		Experiment.
C_{10}	120	75·94	76·56
H_{10}	10	6·32	6·85
N_2	28	17·74	—
	158	100·00	

This base is a well-defined diamine. It is very soluble in

alcohol, ether, and benzole. It boils at a very high temperature, which I believe to be above the limits of the mercurial thermometer.

Hydrochlorate of Naphthyldiamine.—The preparation of this salt has already been given. It is very difficult to obtain perfectly pure, as small quantities of the hydrochlorate of naphthylamine cling to it with great obstinacy, thus rendering it difficult to obtain satisfactory results on analysis; because, as naphthylamine is a monamine and this new base a diamine, the presence of a little of the hydrochlorate of the former greatly reduces the percentage of the chlorine and at the same time raises that of the carbon and hydrogen.

Specimens dried at 100° C. and burnt with chromate of lead gave the following numbers:—

I. ·3620 of substance gave
·6921 of CO_2 and
·1805 of H_2O.
II. ·3363 of substance gave
·6452 of CO_2 and
·1652 of H_2O.
III. ·3774 of substance gave
·7239 of CO_2 and
·1914 of H_2O.
IV. ·3696 gave
·4471 of AgCl.

Percentage composition:—

	I.	II.	III.	IV.
Carbon.....	52·14	52·32	52·31	—
Hydrogen ..	5·54	5·45	5·63	—
Chlorine	—	—	—	29·92

The formula—

$$C_{10}H_{10}N_2,2HCl$$

requires the following numbers.

	Theory.		Mean of experiment.
C_{10}	120	51·95	52·25
H_{12}	12	5·20	5·54
N_2	28	12·12	—
Cl_2	71	30·73	29·92
	231	100·00	

This salt is moderately soluble in water, and crystallizes from its boiling solution in small plates. It is thrown down almost entirely from its aqueous solutions by the addition of an excess of hydrochloric acid. It is very nearly insoluble in alcohol. When pure it is white, but generally appears of a drab colour from oxidation. Its solutions possess a burning taste. With bichloride of platinum and terchloride of gold, this hydrochlorate produces dirty green precipitates, evidently products of oxidation.

Sulphate of Naphthyldiamine.—This substance is best obtained by adding dilute sulphuric acid to a boiling saturated solution of the hydrochlorate, when, in a few moments, the new salt will commence crystallizing out, sometimes in long needles, arranged from a centre. Thus obtained, it is to be collected upon a filter and washed until free from acid, or it may be re-crystallized. This salt generally presents itself as a white, but sometimes as a pale brown crystalline powder, which is nearly insoluble in cold water; re-crystallization is apt to render it impure, owing to oxidation. Its colour may often be improved by washing with ether. It appears to be insoluble in alcohol. Specimens dried at 100° C. and burnt with chromate of lead gave the following numbers:—

I. ·3053 of substance gave
·5239 of CO_2 and
·1306 of H_2O.

II. ·3423 of substance gave
·5880 of CO_2 and
·1527 of H_2O.

III. ·3952 of substance gave
·3566 of $BaSO_4$.

IV. ·3466 of substance gave
·3180 of $BaSO_4$.

V. ·5575 of substance gave
53 c.c. of moist nitrogen at 15° C, and 756 m.m.
corrected vol. = 49·13 c.c. = ·0617 grm. of nitrogen.

Percentage composition:—

	I.	II.	III.	IV.	V.
C	46·80	46·84	—	—	—
H	4·75	4·95	—	—	—
SO_4	—	—	37·4	37·8	—
N	—	—	—	—	11·06

The formula—

$$C_{10}H_{10}N_2,H_2SO_4$$

requires the following numbers:—

	Theory.		Mean of experiment.
C_{10}	120	46·87	46·82
H_{12}	12	4·69	4·85
N_2	28	10·94	11·06
SO_4	96	37·50	37·60
	256	100·00	

This salt dissolves in Nordhausen sulphuric acid; and, if gently warmed, produces a difficultly soluble sulpho-acid, which body has not yet been analysed.

Nitrate of Naphthyldiamine.—The best method of obtaining this salt is to boil a solution of nitrate of strontium with the sulphate of naphthyldiamine in equivalent proportions, filtering the solution and evaporating it over sulphuric acid *in vacuo*. Thus obtained, it presents itself as a crystalline warty mass, which, if left in a moist atmosphere, quickly turns black.

Oxalate of Naphthyldiamine.—This salt crystallizes in small tufts.

An alcoholic solution of naphthyldiamine when mixed with a solution of nitrate of silver, produces a white precipitate, which immediately changes to a dull green-coloured mass, with separation of metallic silver.

With perchloride of mercury, this base produces a yellowish precipitate which on drying, even under the air pump, rapidly decomposes and turns green.

When an alcoholic solution of naphthyldiamine is mixed with bisulphide of carbon, sulphuretted hydrogen is gradually disengaged, and in the course of a week small dark-coloured crystals are deposited, which, under the lens, appear transparent, and of a garnet colour; they are nearly insoluble in alcohol, ether, and benzole, imparting only a pale-yellow colour to these solvents. These solutions are very fluorescent, and upon the addition of a drop of hydrochloric acid, become much more so, the solution at the same time becoming of a light magenta tint. The fluorescence is not very unlike gold that has been slowly precipitated. The mother-liquors from this substance, on being slowly evaporated, deposit brilliant colourless plates of a second body.

The most characteristic property of naphthyldiamine is its

behaviour with oxidizing agents. If to a solution of any of its salts a dilute solution of nitrite of potassium, perchloride of iron, bichromate of potassium, or ferricyanide of potassium be added, it immediately produces, in very dilute solutions, a magnificent green coloration; or, in moderately strong ones, a beautiful flocculent green precipitate. The delicacy of this reaction is remarkable, for if only a few drops of a solution of the hydrochlorate of this base be added to a pint of water, and then treated with ferricyanide of potassium, the whole will assume a pale-green colour. I have not attempted to establish the composition of this green substance; with ammonia, it changes in colour to a dull violet, and with hydrochloric acid, to a brownish red; when submitted to destructive distillation, either alone or with potash, naphthyldiamine is regenerated.

The formation of this green product by means of oxidizing agents, acts as a very distinctive test between naphthyldiamine and its isomer naphthene-diamine, the latter substance producing, under the same circumstances, only a purple-brown or maroon coloration, according to the proportion of acid present.

The mother-liquors, from the crystallized mixture of naphthylamine and naphthyldiamine previously mentioned, besides containing a small quantity of the two last-named bases, also contain ammonia and a nitrile base. To separate these I distilled the mother-liquors with excess of caustic potash until all bases easily volatilized had passed over, the product being collected in a receiver containing dilute hydrochloric acid. The contents of the receiver were then evaporated to dryness, and the residue exhausted with absolute alcohol to separate chloride of ammonium. This alcoholic solution was evaporated to dryness, and the resulting product treated with fuming nitric acid to destroy any naphthylamine or naphthyldiamine. It was then redistilled with potash, the distillate being collected as before in dilute hydrochloric acid and then evaporated to dryness, and, after being again exhausted with alcohol to separate a further quantity of chloride of ammonium, again evaporated to dryness.

The syrupy product thus obtained was dissolved in water and mixed with a solution of bichloride of platinum: at first some ammoniochloride of platinum came down, but on carefully evaporating the mother-liquor over sulphuric acid, a beautifully crystallized salt was obtained, which, when washed with alcohol and

ether and dried at 100° C., gave the following number upon ignition :—

·1062 of substance gave
·0372 of platinum = 35·02 per cent.

This closely agrees with that required by the platinum salt of pyridine, viz., 34·6 p.c.

As it was very important to prove that this salt was really a platinum salt of pyridine, I boiled a quantity of it thoroughly with water for two days. By this means I obtained the characteristic so-called bihydrochlorate of platinopyridine as a sulphur-yellow precipitate, which was well washed with boiling water and then dried at 100° C. Combustions of two different preparations gave the following numbers :—

I. ·3856 of substance gave
·3386 of CO_2 and
·0757 of water.
II. ·3834 of substance gave
·3376 of CO_2 and
·0772 of H_2O.
III. ·2019 of substance gave
·0795 of platinum.
IV. ·1780 of substance gave
·0703 of platinum.

Percentage composition :—

	I.	II.	III.	IV.
Carbon	23·94	24·01	...	—
Hydrogen ..	2·18	2·23	—	—
Platinum ..	—	—	39·37	39·49

The formula

$$C_5H_5N,Pt,Cl_2$$

requires the following values :—

	Theory.		Experiment.
C_5	60·	24·12	23·98
H_5	5·	2·01	2·20
N	14·	5·64	—
Pt	98·7	39·68	39·43
Cl_2	71·0	28·55	—
	248·7	100·00	

I believe this is the first instance of the formation of a nitrile base of this class by any other process than that of destructive distillation.

The formation of two of the bases described in this paper is rather remarkable. I now speak of naphthyldiamine and pyridine. The base from which these are formed, viz., azodinaphthyldiamine, has been shown to be built up in the following manner :—

$$\left.\begin{matrix} C_{10}H_7 \\ C_{10}H_7 \\ N''' \\ H \end{matrix}\right\} N_2.$$

At any rate it has been shown to be formed of two equivalents of naphthylamine, linked together by triatomic nitrogen replacing two atoms of hydrogen in one molecule and one atom of hydrogen in the other molecule of naphthylamine, therefore leaving only one atom of replaceable hydrogen. We have seen that this body, when treated with nascent hydrogen, yields, amongst other bases, the base I have named, naphthyldiamine. Now it is evident, or at any rate we have no instances on record, that nascent hydrogen will remove hydrogen from a radical. Hence we cannot assume that this new base contains a radical with less hydrogen than $C_{10}H_7$, and it cannot therefore have the same constitution as naphthylene-diamine, which contains $C_{10}H_6$. We generally view $C_{10}H_7$ as monatomic, but a monatomic radical cannot bind two equivalents of ammonia together, and produce a diamine like this new base. If we consider naphthalene and its derivatives, we find that it combines with either two or four equivalents of chlorine or bromine, thereby showing it to be either di- or tetratomic, according as the reagent is given in excess or not; therefore as naphthyl contains one atom of hydrogen less than naphthalene, it may be not only mono-, but also tri- or pent-atomic; and I think this reasoning cannot be regarded as violent, because we find C_3H_5 in allylamine and allylic alcohol acting as a monatomic radical, and in glycerine as a triatomic radical. Therefore I think in this instance we may be justified in assuming this new base to contain $C_{10}H_7$, acting a triatomic part this would make it to be constituted thus :—

$$\left.\begin{matrix} C_{10}H_7''' \\ H_3 \end{matrix}\right\} N_2,$$

Naphthene-diamine being

$$\left.\begin{matrix} C_{10}H_6'' \\ H_4 \end{matrix}\right\} N_2.$$

It is on account of these considerations that I have termed it naphthyldiamine.

Its formation may be expressed thus—

$$\left.\begin{matrix} C_{10}H_7 \\ C_{10}H_7 \\ N''' \\ H \end{matrix}\right\} N_2 + 2HH = \left.\begin{matrix} C_{10}H_7''' \\ H_3 \end{matrix}\right\} N_2 + \left.\begin{matrix} C_{10}H_7 \\ H_2 \end{matrix}\right\} N.$$

Azodinaphthyldiamine. Naphthyldiamine. Naphthylamine.

The formation of pyridine appears to be most remarkable; truly it is only produced in small quantities, but it is invariably formed. Here we have a base containing only C_5, produced from a base containing no radicals with less than C_{10}. Had its production resulted from the action of powerful oxidising agents, one would not have been surprised, seeing that carbon might have passed off as carbonic acid, but in this instance it has been quietly produced by the action of nascent hydrogen, at the boiling point of alcohol only. It would therefore appear that the naphthyl had combined with three equivalents of hydrogen and then broken up into two equivalents of C_5H_5, the radical supposed to exist in pyridine. It is perhaps worth remarking that the formula of pyridine is exactly half that of napthyl-diamine; this consideration induced me to make several experiments, to see if it were possible to split it up into that base, but as yet my results have been unsuccessful.

I have made some experiments upon the action of nascent hydrogen, on the product corresponding to azodinaphthyldiamine belonging to the phenyl series, obtained by Griess. It appears that substances similar to those described in this paper are produced, I have also found that in the reduction of nitronaphthalene, dinitronaphthalene, nitrobenzole, and dinitrobenzole by means of nascent hydrogen, minute quantities of nitrile bases are produced.

XXVIII.—*On a Mode of Measuring the Relative Sensitiveness of Photographic Papers.*

By Arthur M'Dougall, B.Sc.

Being the results of the investigation for which the Dalton Chemical Scholarship at Owens College was awarded,

OCTOBER 1864.

Up to the present time no attempt has been made to represent quantitatively the changes in tint produced upon photographically prepared papers when exposed to a known amount of light, or to express in terms of a given standard the sensitiveness of any of the photographic preparations. At Professor Roscoe's suggestion I have endeavoured to take the first step towards the attainment of a knowledge of these quantitative relations by determining the relative sensitiveness of photographic papers prepared with varying quantities of different sensitising agents, defining relative sensitiveness to be represented by the reciprocals of the times during which the several papers must be exposed to a constant source of light in order that they may all attain the same tint as determined by the monochromatic soda flame. As, however, it is clearly impossible to determine directly the exact times during which papers of different degrees of sensitiveness must be exposed to light, in order that each shall attain precisely the same tint, use was made of the law established by Professors Bunsen and Roscoe in their last paper on photochemical measurements,* viz., that equal degrees of tint upon sensitive chloride of silver paper are produced by equal products of the intensity of the acting light into the time of exposure,—light of the intensity 50, for example, acting for the time 1, producing the same blackening effect as light of the intensity 1 acting for the time 50.

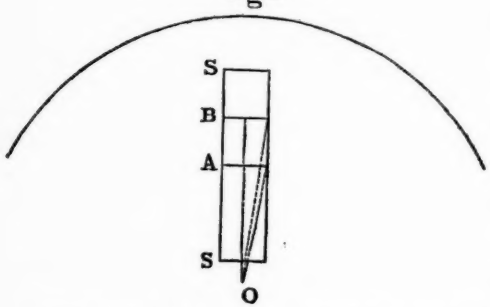
According to the method of measurement founded upon this law, the relative sensitiveness of the different papers can be determined by exposing them for the same time, or for different known times, to the action of a constant source of light, and by comparing the tints thus obtained with the positions of identical shade upon a strip of paper prepared in the pendulum photometer (Phil. Trans. 1863, p. 140). By reference to Table I. of the above mentioned paper the relative times of exposure are obtained which were needed to produce the tints in question upon the standard paper,

* Phil. Trans. 1863, p. 139.

the reciprocals of these times give, then, according to our definition, the relative sensitiveness of the papers. In most cases it is necessary that the times of exposure of the various papers be made different, in order that each paper shall attain one of the requisite tints, and not become either too light or too dark. The results obtained from the table must, in these cases, be multiplied by the reciprocals of the times of exposure, in order that the required sensitiveness may be obtained. It thus becomes necessary to determine the relation of these times of exposure with a greater degree of accuracy than can be attained by merely uncovering and covering the papers by the hand. This is effected by exposing the papers in an instrument, which may be termed the disc photometer, by means of which, not only the papers can be exposed with accuracy for different known times, varying from 1·00 to 3·11, but any errors arising from variation in the intensity of the daylight are eliminated.

The instrument consists of a metallic disc 353 mm. in diameter, having a rectangular slit 48 mm. wide by 144 mm. long, cut out at a distance of 15·5 mm. from the centre of the disc, as represented at SS, Fig. 1. The disc rotates upon a vertical axis, so that it can be made to pass horizontally close above the sensitised papers, which are placed upon a block at known distances from the centre of the disc, along a line parallel to a radius of the circular disc. The relative times during which the several papers will be exposed on every revolution of the disc, can be calculated when the distance of the papers from the centre of the disc and the breadth of the slit are given. Thus, if A and B, Fig. 1, represent two pieces of paper placed at the distances a and b from the centre O of the disc; and if the breadth of the slit be c, we have

Fig. 1.



$$\frac{\text{The time of exposure of paper A}}{\text{The time of exposure of paper B}} = \frac{\sin^{-1}\frac{\frac{1}{2}c}{b}}{\sin^{-1}\frac{\frac{1}{2}c}{a}}$$

The following numbers, giving the relative times of exposure in the disc photometer for each 10 mm. are thus calculated :—

Distance from centre of disc.	Time.	Distance from centre of disc.	Time.
150 mm.	1·000	90 mm.	1·678
140 „	1·071	80 „	1·895
130 „	1·154	70 „	2·175
120 „	1·251	60 „	2·551
110 „	1·367	50 „	3·112
100 „	1·506		

An experiment thus made for the purpose of determining the relative sensitiveness of the photographic papers A and B, which were exposed in the disc apparatus, gave $a = 52{\cdot}8$mm., $b = 76{\cdot}8$mm. On reading off the points on a pendulum strip identical in shade with A and B after exposure, the position of A was found to be 141 mm. corresponding to the time 0·482, and that of B 129·7 mm. corresponding to the time 0·540; hence the fractions $\frac{1}{482}$ and $\frac{1}{540}$ would represent the relative sensitiveness of the papers if they had both been exposed for an equal length of time. They were, however, exposed in the disc photometer for different times, and the relations of these times is found by the expression

$$\frac{\sin^{-1}\frac{24}{52{\cdot}8}}{\sin^{-1}\frac{24}{76{\cdot}8}} = 1{\cdot}484$$

and the relative sensitiveness of the papers A and B is as the numbers

$$1 \;:\; \frac{1{\cdot}484 \times 0{\cdot}540}{0{\cdot}482} = 1{\cdot}66.$$

In like manner the relative sensitiveness of any number of papers can be determined, provided (1) that the papers prepared with varying quantities of salts each possess the same degree of sensitiveness throughout their surface, and (2) that the disc photometer is found to fulfil its functions.

For the purpose of ascertaining whether the first of these conditions holds good, sheets of the best white photographic paper, 0·04 of a square metre in area, were salted by immersion in solutions containing in 100 parts the following quantities of pure chloride of sodium: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, and 20 parts by weight. The papers salted in these different solutions were then silvered by floating for five minutes on a bath of nitrate of

silver, containing 12 per cent. of silver salt. Three pieces were cut from each sheet when dry, 80 mm. apart, from the top, middle, and bottom of the sheet as it had been hung up to dry, and the three pieces exposed simultaneously to daylight. The tint which each paper had assumed was then read off upon a pendulum strip. The following numbers give the mean of ten separate readings made for each paper upon the millimetre scale of the pendulum strip, and the close agreement of the numbers in each experiment shows that the whole of each sheet of paper possesses a uniform degree of sensitiveness, the slight differences observed in the readings being due to errors of experiment:—

	1 p.c. Na.Cl.		2 p.c. Na.Cl.		3 p.c Na. Cl.		4 p.c. Na.Cl.		5 p.c. Na.Cl.	
	Exp.1	Exp.2	Exp.1	Exp.2	Exp.1	Exp.2	Exp. 1	Exp. 2	Exp. 1	Exp. 2
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
Top of sheet ...	133·6	109·5	129·0	109·2	81·0	132·6	133·8	147·1	135·4	138·0
Middle of sheet.	132·0	108·6	130·0	109·0	80·0	131·7	134·5	148·1	134·7	139 3
Bottom of sheet	132·0	109·0	130·0	107·5	78·6	131·9	133·0	148·0	130·0	134·9

	6 p. c. Na.Cl	7 p.c. Na.Cl	8 p. c. Na.Cl	9 p. c. Na.Cl	10 p. c. Na. Cl.			15 p. cent. Na. Cl.	20 p.c. Na. Cl.	
					Exp.1	Exp.2	Exp. 3		Exp. 1	Exp. 2
	mm.	mm.	mm.	mm.	mm.	mm.	mm	mm.	mm.	mm.
Top of sheet...	134·0	89·3	138·0	141·4	88·0	130·4	121·8	107·7	141·8	133·6
Middle of sheet	132·5	86·6	134·0	138·4	91·0	128·8	120·0	106·0	143·0	133·8
Bottom of sheet	131·0	86·0	132·5	139·1	90·0	132·5	120·7	107·0	138·0	133·2

In order to ascertain the degree of accuracy which can be attained in measurements made with the disc photometer, a strip of paper salted in a three per cent. chloride of sodium solution, and silvered in the standard silver bath, was placed along the whole length of the slit, and afterwards insolated by the rotation of the disc. Portions of the paper thus exposed were then cut off at known distances along the slit, the tint of each compared with that of a pendulum strip, and the sensitiveness then calculated according to the formula given above. If the instrument works properly, the numbers thus obtained, expressing the relative sensitiveness of the various points of the paper, must be identical; that this is nearly the case is seen from the following table, giving the results of seven experiments made in this manner:—

Expt. I.		Expt. II.		Expt. III.		Expt. IV.		Expt. V.		Expt. VI.		Expt. VII.	
Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.	Distance on slit.	Relative sensitiveness.
mm.		mm.		mm.		mm.		mm.		mm.		mm.	
60	0·912	57	0 952	47·7	1 ·004	69 ·0	1 ·010	80	1 ·014	102	0 ·950	95	1 ·000
75	1·040	80	1·065	67·	1 ·000	85 ·5	1 ·000	102	1 ·000	121	1 ·008	108	0 ·977
90	1·007	92	0·865	86·5	0 ·996	103 ·0	0 ·991	120	1 028	137·5	1 ·046	122	1 025
105	1·000	111	1·000	106·	0 ·946	124 ·5	0 ·990	135	0 ·956				
120	0·949	125	1·040	142·5	1 ·054								
mean	0·982	mean	0·984	mean	102·0	mean	0 998	mean	0·999	mean	0·999	mean	0·984

A comparison of the numbers of each experiment shows that the mean error is not greater than can be fairly anticipated in such determinations. As a second means of testing the trustworthiness of the instrument, portions of three chloride of silver papers, A, B, and C, of different degrees of sensitiveness, were tinted by exposure in the disc photometer, whilst other pieces of the same papers were insolated for known times by uncovering and covering them by hand, when the sky was cloudless, and in both cases the relative sensitiveness of the papers was determined by reading off upon a pendulum strip in the ordinary manner. The following gives the results of these measurements.

(1.) *Insolation in Disc Photometer.*

Expt.	Relative sensitiveness. Paper A.	Paper B.	Paper C.
No. 1	1·00	1·75	2·74
No. 2	1·00	2·46	3·20
No. 3	1·00	2·53	2·68
No. 4	1·00	2·31	2·75
No. 5	1·00	2·29	3·18
No. 6	1·00	2·63	3·32
No. 7	1·00	2·16	3·73
Mean ..	1·00	2·30	3·09

(2.) *Insolation by Direct Exposure.*

Expt.	Relative sensitiveness. Paper A.	Paper B.	Paper C.
No. 1	1·00	2·38	3·04
No. 2	1·00	2·25	2·76
No. 3	1·00	2·41	3·82
No. 4	1·00	2·22	3·29
No. 5	1·00	2·36	3·09
Mean ..	1 00	2·30	2·96

Determination of the Relative Sensitiveness of Papers Salted in Solutions of different Salts of varying strength.

The first series of measurements was made for the purpose of ascertaining the relative sensitiveness of photographic paper salted in solutions of pure chloride of sodium, containing in 100 parts quantities varying from 0·25 to 20·0 parts of salt, and all silvered in a silver bath containing 12 per cent. of nitrate. As it was impossible to expose this whole set of papers at one time in the photometer owing to the great difference in their sensitiveness, the several series of papers prepared in the solutions containing from 0·25 to 1·75 per cent. of salt, from 1 to 4 per cent., from 1 to 7 per cent., and from 7 to 20 per cent., were insolated at one time in the disc photometer, and the numbers afterwards reduced to the sensitiveness of the 1 per cent. solution taken as the unit. The following table gives the data of six experiments made with the 1, 2, 3, and 4 per cent. papers; the numbers obtained, as a mean of ten readings, for the relative sensitiveness were:

Paper.	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 4.	Expt. 5.	Expt. 6.	Mean.
1 per cent...	1·00	1·00	1·00	1·00	1·00	1·00	1·00
2 per cent...	1·86	1·66	1·89	1·84	1·63	1·84	1·79
3 per cent...	2·22	2·12	2·63	2·45	2·35	2·19	2·33
4 per cent...	3·23	3·21	3·29	3·27	3·11	3·06	3·19

In like manner the relative sensitiveness of the remaining papers was found, the mean of at least six separate experiments being

taken. The following table contains the experimental results of determinations thus made for papers salted in the accompanying amounts of chloride of sodium.

RELATIVE SENSITIVENESS OF PAPERS PREPARED WITH VARYING QUANTITIES OF CHLORIDE OF SODIUM AND CONSTANT EXCESS OF NITRATE OF SILVER.

Percentage of Chloride of Sodium.	Relative Sensitiveness.	Percentage of Chloride of Sodium.	Relative Sensitiveness.
0·25	0·448	6·0	4·45
0·50	0·782	7·0	4·75
1·0	1·000	8·0	4·98
1·5	1·29	9·0	5·24
2·0	1·79	10·0	5·69
3·0	2·33	15·0	6·81
4·0	3·19	20·0	7·20
5·0	3·85		

Determinations were next made with pure chloride of potassium, papers being salted in solutions containing in 100 parts, 0·5, 1·0, 2·0, 4·0, and 7·0 parts of the salt, and silvered in the 12 per cent. nitrate bath.

The following numbers were obtained as a mean of three separate sets of experiments made on different days with different papers:

Strength of Chloride of Potassium solution.	Relative Sensitiveness.
0·5 per cent.	0·815
1·0 „	1·000
2·0 „	1·48
4·0 „	2·56
7·0 „	5·26

By graphical interpolation the following table is calculated:

RELATIVE SENSITIVENESS OF PAPERS PREPARED WITH CHLORIDE OF POTASSIUM.

Percentage of Chloride of Potassium.	Relative Sensitiveness.	Percentage of Chloride of Potassium.	Relative Sensitiveness.
0·5	0·800	4·0	2·50
1·0	1·000	5·0	3·30
1·5	1·20	6·0	4·15
2·0	1·45	7·0	5·20
3·0	1·95		

Papers salted in chloride of ammonium solutions and then silvered gave the following results, as the mean of four sets of experiments:

Strength of Chloride of Ammonium solution.	Relative Sensitiveness.
0·5 per cent.....	0·50
1·0 „	1·00
2·0 „	1·56
4·0 „	3·38
8·0 „	5·87

By graphical interpolation the following table is calculated:

RELATIVE SENSITIVENESS OF PAPERS PREPARED WITH CHLORIDE OF AMMONIUM.

Percentage of Chloride of Ammonium.	Relative Sensitiveness.	Percentage of Chloride of Ammonium.	Relative Sensitiveness.
0·5	0·46	4·0	3·40
1·0	1·00	5·0	4·15
1·5	1·30	6·0	4·80
2·0	1·50	7·0	5·40
3·0	2·35	8·0	5·90

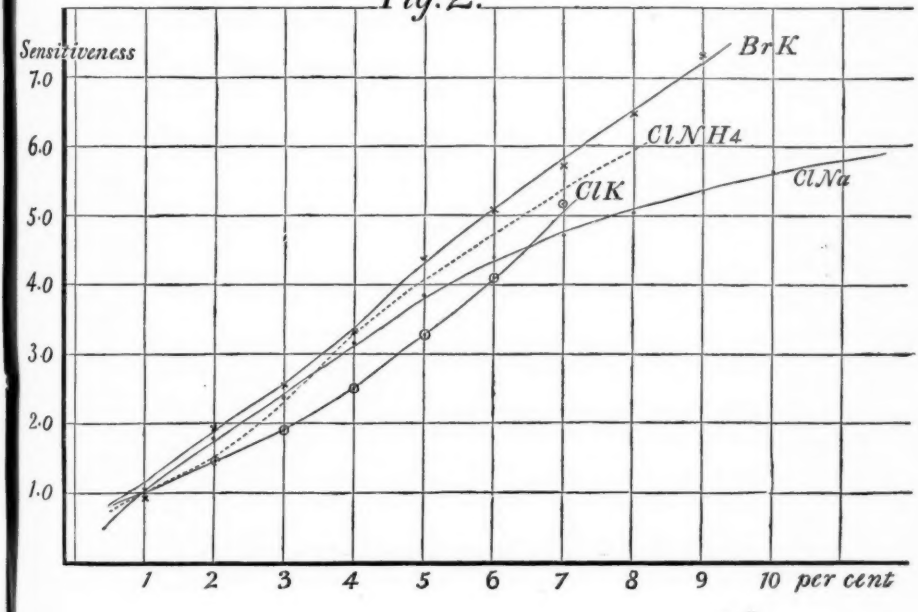
The following numbers were obtained as the mean of seven experiments on paper prepared with bromide of potassium:

RELATIVE SENSITIVENESS OF PAPERS PREPARED WITH BROMIDE OF POTASSIUM.

Percentage of Bromide of Potassium.	Relative Sensitiveness.	Percentage of Bromide of Potassium.	Relative Sensitiveness.
0·25	0·345	5·0	4·41
0·50	0·767	6·0	5·10
1·0	1·00	7·0	5·74
2·0	1·88	8·0	6·49
3·0	2·59	9·0	7·36
4·0	3·34		

The four curves on Fig. 2 represent graphically the above determinations, and from these we see that the rate of increase of sensitiveness with increase of strength of the saline solution is different for the different salts; thus, whilst the sensitiveness of bromide of potassium paper increases nearly proportionally to the quantity of salt added up to 9 per cent., the sensitiveness of chloride of sodium paper prepared from 5 to 20 per cent. solutions, increases in a very much less ratio.

Fig. 2.



Iodide of potassium paper sensitised with excess of silver was so slightly blackened by insolation that it was found impossible to determine the relative sensitiveness of this paper.

Having ascertained the rate of increase of sensitiveness with increase in the strength of the salting solutions, it appeared of interest to determine the action of different salts containing the same quantity of haloid. For this purpose solutions were prepared containing the same quantity of chlorine combined with different metals, and papers salted in these, and afterwards silvered in the standard bath, were exposed to light at the same time, the tint of each paper being read off upon a pendulum strip.

	Relative Sensitiveness.			
	Expt. 1.	Expt. 2.	Expt. 3.	Mean.
Chloride of sodium	1·47	1·50	1·53	1·50
Chloride of potassium	1·60	1·48	1·52	1·53
Chloride of ammonium.....	1·60	1·47	1·53	1·53
Chloride of barium	1·60	1·51	1·58	1·56

A similar series made with bromides gave the same results.

	Relative Sensitiveness.				
	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 4.	Mean.
Bromide of sodium	1·38	1·40	1·54	1·39	1·43
Bromide of potassium	1·42	1·32	1·41	1·30	1·36
Bromide of ammonium.....	1·44	1·34	1·48	1·40	1·41
Bromide of barium	1·39	1·40	1·44	1·39	1·40
Bromide of quinine	1·43	1·41	1·51	1·37	1·43

The foregoing results show that the sensitiveness of papers containing the same quantity of chlorine and bromine combined with sodium, potassium, ammonium, and barium is constant within the limit of experimental error, and, therefore, that the influence of the metal upon the sensitiveness of the papers is not appreciable.

XXIX.—*On some Compounds and Derivatives of Glyoxylic Acid.*

By Henry Debus, PhD., F.R.S.

[From the Philosophical Transactions, 1863, p. 437.]

Organic substances of simple composition, like marsh-gas, ethylene, alcohol, and acetic acid, are deserving of most careful study, not merely on account of their being representative members of numerous and important classes of bodies, but also because they form connecting links between the compounds of inorganic chemistry and the more complicated forms of organic nature.

Glyoxylic acid belongs to this class of bodies, because it bears the same relation to oxalic acid that sulphurous acid does to sulphuric acid, and because it stands to glycollic acid as common aldehyde, C_2H_4O, does to alcohol, C_2H_6O. These relations suggested the experiments which will be described in the following pages.

Combinations of Glyoxylates and Sulphites.

a. Glyoxylic Acid and Bisulphite of Soda.

If a concentrated solution of bisulphite of soda be mixed with one-fourth of its volume of nearly anhydrous glyoxylic acid, a white crystalline precipitate will separate from the mixture in the course of a day or two. This precipitate is to be collected on a filter, washed with cold water, and recrystallized from its solution in the smallest possible quantity of hot water.

The substance thus prepared presents itself in small colourless crystals, which dissolve easily in water, and evolve sulphurous acid with sulphuric acid. The aqueous solution is not altered by the addition of potash or ammonia, but yields a copious white precipitate with acetate of lead. The solid substance, heated on a piece of platinum foil, burns without any unusual appearance.

Analysis shows that it is a compound of glyoxylate of soda with bisulphite of soda, represented by the formula $C_2HNaO_3 . SHNaO_3$.

b. Glyoxylate of Lime with Bisulphite of Lime.

Glyoxylate of lime dissolves rapidly in a saturated solution of sulphurous acid. If this solution be concentrated on the water-bath, and afterwards allowed to stand in the exsiccator, a fine crop of colourless crystals separates. These crystals have to be purified by recrystallization from water, and dried over sulphuric acid *in vacuo*.

This substance, like the soda-compound, dissolves easily in water, and its concentrated solution comports itself with reagents as follows:—Sulphuric acid produces a white precipitate of sulphate of lime and liberates sulphurous acid; lime-water, chloride of barium, and ammonia respectively cause the formation of a white precipitate, whilst carbonate of lime has no decomposing influence. The form of the crystals could not be determined.

Analysis shows that it is a double salt of bisulphite and glyoxylate of lime, containing $2(C_2HNaO_3.SHCaO_3)$, $5H_2O$.

Considering the mode of preparation, the mother-liquor of the salt ought to contain glyoxylic acid. In order to ascertain its presence by experiment, the mother-liquor was evaporated to dryness on the water-bath and the residue exhausted with alcohol. The latter had dissolved an acid which yielded, when treated with carbonate of lime, a salt that contained no sulphur and would not crystallize, but which in other respects comported itself like glyoxylate of lime.

If a compound be the derivative of a substance of an easily changeable nature, its composition, as represented by its rational formula, should always be checked by special experiments. It therefore appeared desirable to regenerate the glyoxylate of lime assumed to form a constituent part of the salt in question. For this purpose an aqueous solution of the latter was mixed with sufficient oxalic acid to precipitate all the lime; the clear filtrate, in order to expel the sulphurous acid, was evaporated on the water-bath till it assumed the consistency of a thin syrup; this residue, which proved to be glyoxylic acid, was dissolved in water and converted, by treatment with chalk, into a crystalline salt that both in form and other properties agreed with glyoxylate of lime.

Glyoxylic acid is a strong acid; it dissolves zinc and expels carbonic acid from carbonates. The experiments described hereafter show that it shares some distinguishing properties with the aldehydes. It may therefore be assumed that, if the acid properties

of glyoxylic acid were less marked, it would combine with the bisulphites like hydride of salicyl.

Compound of Glyoxylate and Lactate of Lime.

Just as glyoxylic acid is formed from ethylic alcohol, so will the homologous acid $C_3H_4O_3$ probably be formed from the alcohol C_3H_8O. But since propylic alcohol is only procurable with great difficulty, I attempted the preparation of $C_3H_4O_3$ from lactic acid.

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} - H_2 = \underset{\text{Pyroracemic acid.}}{C_3H_4O_3}.$$

Two experiments made with nitric acid of 1·2 sp. gr. and lactic acid did not give the desired result. At a low temperature no action appeared to take place, and at a higher temperature, or with more concentrated nitric acid, only the formation of oxalic acid could be expected.

It is well known that platinum when alloyed with silver is dissolved by nitric acid. It therefore appeared not unlikely that lactic acid, when mixed with alcohol, would be oxidized at a moderate temperature by nitric acid. The experiment was made with a mixture of equal weights of lactic acid and alcohol and a suitable quantity of nitric acid, on the plan which I employed for the preparation of glyoxylic acid. An acid was thus obtained which, when treated with lime, furnished neither glyoxylate nor lactate of lime. The salt obtained was white and crystalline, required more boiling water for its solution than either C_2HCaO_3 or $C_3H_5CaO_3$, and when the hot solution cooled, separated therefrom in white crystalline crusts.

Analysis led to the formula $C_5H_8Ca_2O_7$, according to which this substance might be composed as follows :—

Glyoxylate of lime	$C_2H\,Ca\,O_3$
Lactate of lime	$C_3H_5Ca\,O_3$
Water	$H_2\quad O$
	$C_5H_8Ca_2O_7$

The following experiments confirm this composition :—The solution of the compound $C_5H_8Ca_2O_7$ yields with lime-water a white precipitate, which immediately after its formation is found

to be soluble in acetic acid; this precipitate, however, after the lapse of some time, or by exposure to a temperature of 212°, becomes insoluble in this acid. The same property distinguishes the soluble glyoxylates.

$$\underset{\text{Glyoxylate of lime.}}{2(C_2HCaO_3)} + CaHO = \underset{\text{Oxalate of lime.}}{C_2Ca_2O_4} = \underset{\text{Glycollate of lime.}}{C_2H_3CaO_3}.$$

If the formula $C_2HCaO_3.C_3H_5CaO_3.H_2O$ be the correct expression of the composition of the salt in question, then a quantity represented by the above formula ought to be decomposed by boiling lime-water into one atom of lactate, half an atom of glycollate, and half an atom of oxalate of lime; and this conclusion is confirmed by experiment.

The last member of the preceding formula may be eliminated by heat; it appears, however, that the remainder, $C_2HCaO_3 + C_3H_5CaO_3$, suffers some change by this process.

The tendency to form this double salt is perhaps the reason why the oxidating influence of the nitric acid only affects the alcohol, and does not extend to the lactic acid.

Ammoniacal Compounds of some Glyoxylates.

a. Glyoxylate of Lime and Ammonia.

Pure and well-crystallized glyoxylate of ammonia was dissolved in the least possible quantity of hot water, and the solution thus obtained was divided into two equal parts. One part, on being mixed with chloride of calcium, assumed the appearance of a transparent jelly, which resembled silicic acid when precipitated by hydrochloric acid from a concentrated solution of silicate of potash; the vessel, in fact, could be inverted without any portion of its contents being lost; after the lapse of a few hours white opaque points were observed in the jelly, which gradually increased in number and magnitude, until at last the whole of the jelly-like substance was converted into a fine crop of prismatic crystals; these were found to agree in form and other properties with glyoxylate of lime.

To the other part of the solution of glyoxylate of ammonia a mixture of chloride of calcium and acetate of ammonia was added. In this instance no immediate change took place, but in the course of twenty-four hours a white precipitate, a compound of glyoxylate of lime and ammonia, made its appearance; the precipitate

was collected on a filter, washed with cold water, and dried over sulphuric acid.

A similar result was obtained by precipitating a solution of glyoxylate of ammonia with acetate of lime, just sufficient ammonia being at the same time added to keep the liquid neutral; the compound thus prepared is colourless or slightly yellow, dissolves sparingly in water, but is easily soluble in dilute acetic acid; it becomes highly electrical when rubbed in a mortar, and burns like tinder on a piece of heated platinum foil, leaving carbonate of lime. The aqueous solution possesses an alkaline reaction, and shows no change on the addition of lime-water.

The analysis of this salt led to the formula $3(C_2HCaO_3),2NH_3,H_2O$.

If, therefore, glyoxylate of ammonia be decomposed by acetate of lime, acetate of ammonia and glyoxylate of lime are formed; the latter, however, withdraws a part of the ammonia from the acetate of ammonia, and thus produces the compound which has just been mentioned. Some grammes of this substance were mixed with oxalic acid solution sufficient to convert two-thirds of its lime into oxalate. If the composition ascribed to the compound be correct, the filtrate from the oxalate of lime ought to contain glyoxylates of lime and ammonia; the filtered liquid was evaporated over sulphuric acid *in vacuo*, when a crust, consisting of small prisms arranged round a common centre, remained. This substance was repeatedly recrystallized from water; and in each process the crystals which formed first, were separated from those which made their appearance after a half or three-quarters of the solution had been evaporated. In this manner two kinds of crystals were obtained: those which separated first, were found to be identical with glyoxylate of lime, while those which formed last possessed the properties of glyoxylate of ammonia. This experiment, therefore, confirms the formula $3(C_2HCaO_3).2NH_3 + H_2O$, which was deduced from analytical results.

A compound of a similar nature may be directly obtained from glyoxylate of lime and ammonia. For this purpose a hot and concentrated solution of $C_2HCaO_3.H_2O$ is to be mixed with a few drops of ammonia, and filtered; ammonia is then to be added to the filtrate so long as a precipitate forms; the latter is to be collected and washed with cold water. The compound, thus prepared, possesses the same properties as the one obtained from glyoxylate of ammonia and acetate of lime, and its composition is represented by the formula $3(C_2HCaO_3).2NH_3$; that is to say,

it differs from the preceding by containing one atom of water less.

If a quantity of this substance be treated with oxalic acid solution, sufficient to convert its lime into oxalate, the supernatant liquid comports itself like a solution of glyoxylic acid and glyoxylate of ammonia.

b. Glyoxylate of Silver and Ammonia.

A concentrated solution of glyoxylate of ammonia yields with nitrate of silver a crystalline precipitate of glyoxylate of silver. But if the solution of glyoxylate of ammonia contain other ammoniacal compounds, such as nitrate of ammonia, the precipitate is found to contain ammonia besides the other components already mentioned.

A specimen prepared under the last-mentioned circumstances and afterwards dried *in vacuo*, was found to consist of $4(C_2HAgO_3)$ $3NH_3-3H_2O$.

The absence of nitric acid in this salt was proved by a special experiment with proto-sulphate of iron and sulphuric acid. The silver could not be determined by simple ignition, because heat decomposes the compound with explosive violence.

c. Glyoxylate of Lead and Ammonia.

Acetate of lead produced, in a liquid containing glyoxylate and acetate of ammonia, a heavy white precipitate, containing $7(C_2HPbO_3).2NH_3-2H_2O$.

This substance, on being pounded in a mortar, became highly electrical.

An ammoniacal solution of crystallized glyoxylate of ammonia, raised to temperatures below 212°, turns brown, and forms derivatives of an acid character; neither these substances, however, nor their salts could be obtained in crystals.

The compounds of ammonia with the glyoxylates are easily decomposed by heat, and by nitric acid and other reagents; the products of decomposition could not be examined, because their physical properties precluded their preparation in a pure state. An experiment, which showed the attraction between glyoxylates and ammonia, may be mentioned here. If a quantity of $3(C_2HCaO_3).2NH_3$ be boiled with caustic potash, a part of the ammonia is very slowly expelled; if the liquid be evaporated to

dryness, and the residue be raised to a higher temperature, it assumes a beautiful purple colour, and at the same time emits streams of ammonia. This red substance is very changeable, and is formed, even under the most favourable circumstances, in but very small quantities.

Action of Hydriodic Acid on Glyoxylates.

Hydriodic acid and glyoxylate of lime were heated together for several days in sealed glass tubes, the temperature varying from 100° C. to 110° C. In order to decompose a part or the whole of the hydriodic acid, the contents of the tubes were exposed for some time to the influence of the atmosphere, and finally saturated with carbonate of lime. The whole was then boiled and filtered, and the filtrate mixed with alcohol. A precipitate was formed which proved to be a quantity of glyoxylate of lime, little inferior to that which was originally taken for the experiment.

Action of Sulphuretted Hydrogen on Glyoxylates.

Through a concentrated solution of glyoxylic acid a current of sulphuretted hydrogen was passed until the liquid appeared to be completely saturated; no perceptible action took place, and even after twenty-four hours' contact the liquid seemed to be unchanged. The solution was now evaporated, at first over pieces of hydrate of potash, and afterwards over sulphuric acid *in vacuo*. As soon as most of the water was gone, small needles, radiating from a common centre, began to form, and at last the whole of the contents of the evaporating basin appeared one mass of crystals, which were found to be soaked with a syrupy mother-liquor, and to be so easily soluble in the ordinary means of solution, that all attempts at further purification were abandoned. A solution of glyoxylate of lime comports itself like glyoxylic acid when acted upon by sulphuretted hydrogen; it apparently remains unchanged; but on allowing a part of it to evaporate at ordinary temperatures *in vacuo*, a brittle, transparent, and amorphous compound is obtained.

In order to avoid the inconvenience of evaporation *in vacuo*, the rest of the glyoxylate-of-lime solution, after having been treated with sulphuretted hydrogen, was mixed with a little more than its bulk of alcohol. Nearly the whole of the new compound sepa-

rated as a precipitate, which was collected on a filter and washed with spirit of wine.

Thus prepared, the substance easily dissolved in water, forming a solution of a pale pink colour. The liquid, after the evaporation of the water *in vacuo*, left a transparent, amorphous and nearly colourless substance. This compound is the lime-salt of an acid which bears a similar relation to glyoxylic acid that thiacetic acid does to acetic acid. In the state of powder it exhibits a striking property when brought in contact with water; it becomes as viscous as glass when rendered red-hot by means of a Bunsen's burner, and may be drawn out in long threads. By degrees the water dissolves the viscous mass, and forms a solution which shows the following properties with reagents:—A white precipitate is formed by the addition of acetate of zinc or corrosive sublimate; acetate of lead or nitrate of silver throws down a yellow precipitate; and sulphate of copper causes the immediate separation of a black substance, which is probably sulphide of copper. Both the silver and the lead precipitates turn black, the silver after the lapse of some time at ordinary temperatures, and the lead at once on exposure to a temperature of 100° C. Hydrochloric acid produces no perceptible change in the aqueous solution of the compound; ammonia causes the formation of a white precipitate; and lime-water the same result as it does with glyoxylate of lime. The brown colour of iodine immediately disappears, as it does in solutions of other sulphur-compounds, such as xanthate of potash. Sesquichloride of iron acts like iodine. The solution of this sulphur-compound, when boiled, decomposes; it turns yellow; a crystalline powder of oxalate of lime separates; and a lime-salt, which could not be obtained in crystals, remains in solution. The compound burns on a hot piece of platinum foil like tinder, and evolves, when heated in a glass tube which is sealed at one end, an odour like that of mercaptan. It gives, by analysis, results agreeing with the formula $C_4H_2Ca_2\left.\begin{matrix}O_5\\S\end{matrix}\right\}. 3H_2O$, and its formation may be represented by the following equation:—

$$2(C_2HCaO_3 + H_2O) + H_2S = C_4H_2Ca_2\left.\begin{matrix}O_5\\S\end{matrix}\right\} + 3H_2O.$$

Glyoxylate of lime.

The crystalline derivative from sulphuretted hydrogen and gly-

oxylic acid just mentioned is probably represented by the formula $C_4H_4{}^{O_5}_{S}\}$.

Neither the salts prepared from this acid, nor the compounds obtained by exchanging the calcium in $C_4H_2Ca_2{}^{O_5}_{S}\} + 3H_2O$ for other metals could be obtained in crystals; and therefore I did not pursue the investigation of these bodies.

Action of Zinc on Glyoxylic Acid.

A concentrated solution of this acid dissolves pure zinc without evolution of hydrogen gas, and the liquid at the same time becomes perceptibly warm; the reaction very soon ceases. Even if metal and acid be left in contact for a day or two at ordinary temperatures, the liquid will still contain a considerable portion of unchanged glyoxylic acid. The process may be accelerated, and may in fact be completed in the course of eight or ten hours, by exposing the reacting substances to a temperature of about 80° C. The previously colourless liquid has assumed a yellow colour, and no longer contains glyoxylic acid or glyoxylate of zinc. The pieces of undissolved zinc are found to be covered with a small quantity of a white crystalline powder. Glyoxylic acid thus saturated with zinc was mixed with pure carbonate of lime and treated with sulphuretted hydrogen: the zinc precipitated as sulphide of zinc, and the liberated acid dissolved carbonate of lime and formed a lime-salt. The filtrate from the zinc-sulphide and the excess of calcic carbonate furnished, on evaporation, only one kind of crystals, which possessed the form of glycollate of lime. After purification by recrystallization from boiling water, and drying over sulphuric acid, they were found to contain 16·5 p. c. calcium and 21·1 water, agreeing therefore with the formula of glycollate of lime, $2(C_2H_3CaO_3).3H_2O$, excepting in the percentage of water, which differs to the amount of nearly 1 per cent. from the theoretical number. I have, indeed, always found the amount of water contained in glycollate of lime which has been dried over sulphuric acid to be a little below the calculated quantity. If, however, from preceding results, the amount of calcium contained in 100 parts of the anhydrous substance be calculated, the number thus obtained agrees with the theoretical percentage of calcium in anhydrous glycollate of lime, viz., 21·05 p.c.

The substance is therefore glycollate of lime. The identity of the glycollic acid obtained by the oxidation of alcohol by means of nitric acid with the acid formed by reducing glyoxylic acid with zinc was demonstrated by the equal solubility in water of their respective lime-salts, 100 pts. water at 12° C. dissolving 0·886 pts. of the former and 0·913 of the latter.

Glycollic acid can be obtained from glyoxylic acid by at least two different ways.

1. By direct addition of hydrogen :—

$$\underset{\text{Glyoxylic acid.}}{C_2H_2O_3} + H_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

2. By the decomposition represented in the following equation :—

$$2(C_2H_2O_3) + H_2O = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + \underset{\text{Glycollic acid.}}{C_2H_4O_3} \ldots\ldots\ldots (1.)$$

Under the influence of zinc the following reactions could take place :—

$$3(C_2H_2O_3) + Zn_4 = \underset{\text{Glycollate of zinc.}}{2(C_2H_3ZnO_3)} + \underset{\text{Glyoxylate of zinc.*}}{C_2Zn_2O_3} \ldots\ldots\ldots (2.)$$

or

$$C_2H_2O_3 + Zn_2 = \underset{\text{Glyoxylate of zinc.}}{C_2Zn_2O_3} + H_2.$$

Glyoxylates which contain more than one atom of metal decompose easily at the temperatures at which the experiments were made, and form compounds of glycollic and oxalic acids.

$$\underset{\text{Glyoxylate of zinc.}}{2(C_2Zn_2O_3)} + 2H_2O = \underset{\text{Glycollate of zinc.}}{C_2H_3ZnO_3} + \underset{\text{Oxalate of zinc.}}{C_2Zn_2O_4} + \left.\begin{matrix}Zn\\H\end{matrix}\right\}O.$$

By combining this and the preceding equation, the action of zinc on glyoxylic acid may at once be represented by the following equation :—

$$2(C_2H_2O_3) + 2H_2O + Zn_4 = \underset{\text{Glycollate of zinc.}}{C_2H_3ZnO_3} + \underset{\text{Oxalate of zinc.}}{C_2Zn_2O_4} + H_4 + \left.\begin{matrix}Zn\\H\end{matrix}\right\}O. \quad (3.)$$

* Proceedings of the Royal Society, ix, 711 ; Ann. Ch. Pharm., cx, 326.

If the reaction takes place according to (2), then by the side of five atoms of glycollate only one atom of oxalate of zinc can be produced; but if according to (3), for every five atoms of glycollate five atoms of oxalate of zinc ought to be formed, and twenty atoms of hydrogen be liberated.

The relative quantities of oxalic acid and glycollic acid formed by the action of zinc on glyoxylic acid were therefore first determined. An unknown quantity of the acid was treated with zinc until the action was complete, and the filtrate from the undissolved metal was divided into two parts. In one part the oxalic acid was determined by the usual method, and the glycollic acid in the other by converting the glycollate of zinc into glycollate of lime, and by evaporating and drying the latter at 100° C.; this could be done because no other substance was present in the liquid. In this way 0·98 grm. of glycollate of lime,* and 0·005 grm. of carbonate of lime from the oxalate were obtained.

A white crystalline powder has been mentioned which settles on the zinc during its action on glyoxylic acid; this powder would contain oxalate of zinc. From its solution in ammonia a precipitate of oxalate of lime was obtained, which gave after ignition, 0·095 grm. of carbonate of lime. The whole of the carbonate of lime obtained from the oxalate weighed therefore 0·1 grm., which corresponds to 0·09 grm. of oxalic acid, $C_2H_2O_4$; the above-mentioned 0·98 grm. of glycollate of lime contain 0·784 grm. of glycolic acid, and, therefore, for every atom of oxalic acid we obtain 10·3 of glycollic acid.

Two other experiments conducted on the same plan gave similar results.

The action of zinc on glyoxylic acid takes place, therefore, according to equation (2).

0·906 grm. of glyoxylic acid gave 0·876 grm. of glycollate of lime, corresponding to 0·7 grm. of glycollic acid, and 0·122 grm. of carbonate of lime, corresponding to 0·109 grm. of $C_2H_2O_4$. If we suppose none of the glyoxylate of zinc, formed according to (2), to be decomposed, then no oxalic acid and only 0·62 grm. of glycollic acid ought to have been obtained; if, however, all the glyoxylate of zinc had been decomposed into glycollate and oxalate of zinc, 0·775 grm. of glycolic acid and 0·183 grm. of oxalic acid

* This glycollate of lime contained 21·4 per cent. of calcium, whereas theory requires 21·05 per cent.

ought to have been found. The actual numbers are intermediate between these two extremes, and consequently half of the glyoxylate of zinc formed from 0·906 grm. of glyoxylic acid, according to equation (2), underwent the decomposition represented in equation (1). The action of zinc on glyoxylic acid may, therefore, be explained as follows :—zinc dissolves and forms glyoxylate of zinc, $C_2Zn_2O_3$; the hydrogen, instead of being liberated, combines with other glyoxylic acid and zinc, and produces glycollate of zinc; a quantity of $C_2Zn_2O_3$, dependent on time and temperature, decomposes into glycollate and oxalate of zinc.

The following experiment proves that no hydrogen is liberated in this reaction. 0·906 grm. of glyoxylic acid and a few pieces of zinc were placed in a flask and the vessel nearly filled with water: a perforated cork holding a bent glass tube was then attached to the mouth of the flask, the other end of the tube being placed under a graduated receiver filled with mercury. The flask was then warmed to nearly 100° C., and kept at this temperature for ten hours, after which time no more gas was given off. The apparatus was found to be air-tight both before and after the experiment. The quantity of the gas which was collected, when measured at 11° C., was 10 cub. centims.; it possessed the properties of atmospheric air. If one atom of hydrogen had been set free for each atom of glyoxylic acid which was taken, the 0·906 grm. of acid ought to have liberated 0·0122 grm. of hydrogen; this quantity measures 135 cub. centims. at 0° C. and 0·76 in. pressure.

Some years ago I directed attention to the following considerations.*

Among the products formed by the action of nitric acid on alcohol, which remain after the more volatile substances have been evaporated on the water-bath, are three acids, glycollic acid, glyoxylic acid, and oxalic acid. These bodies show the same differences in composition as benzylic alcohol, oil of bitter almonds, and benzoic acid.

C_7H_8O	$C_2H_4O_3$
Benzylic alcohol.	Glycollic acid.
C_7H_6O	$C_2H_2O_3$
Oil of bitter almonds.	Glyoxylic acid.

* Quarterly Journal of the Chemical Society, vol xii, p. 234.

$C_7H_6O_2$ Benzoic acid. $C_2H_2O_4$ Oxalic acid.

They comport themselves with different reagents like the members of the benzoyl series. Hydrate of potash decomposes glyoxylic acid into glycollic and oxalic acids, and oil of bitter almonds into benzylic alcohol and benzoic acid; dilute nitric acid oxidizes glyoxylic acid to oxalic acid, and oil of bitter almonds to benzoic acid.

a. Decomposition with potash:—

$$\underset{\text{Oil of bitter almonds.}}{2C_7H_6O} + H_2O = \underset{\text{Benzylic alcohol.}}{C_7H_8O} + \underset{\text{Benzoic acid.}}{C_7H_6O_2}$$

$$\underset{\text{Glyoxylic acid.}}{2C_2H_2O_3} + H_2O = \underset{\text{Glycollic acid.}}{C_2H_4O_3} + \underset{\text{Oxalic acid.}}{C_2H_2O_4}$$

b. Oxidation with nitric acid:—

$$\underset{\text{Oil of bitter almonds.}}{C_7H_6O} + O = \underset{\text{Benzoic acid.}}{C_7H_6O_2}$$

$$\underset{\text{Glyoxylic acid.}}{C_2H_2O_3} + O = \underset{\text{Oxalic acid.}}{C_2H_2O_4}$$

According to Friedel, oil of bitter almonds unites with hydrogen and forms benzylic alcohol; and the experiments described in this paper show glyoxylic acid to enter into combination with this element, forming glycollic acid.

$$\underset{\text{Oil of bitter almonds.}}{C_7H_6O} + H_2 = \underset{\text{Benzylic alcohol.}}{C_7H_8O}$$

$$\underset{\text{Glyoxylic acid.}}{C_2H_2O_3} + H_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

Glycollic acid may, therefore, be termed the alcohol of oxalic acid, and glyoxylic acid the aldehyde of both; in fact, glyoxylic acid possesses other properties which are generally only found in connexion with aldehydes. Amongst these are the great affinity of glyoxylates for sulphites (whereby well-defined and beautifully crystallising compounds are formed), the exchange of the oxygen of the acid for the sulphur of sulphuretted hydrogen, and, finally, the production of compounds with ammonia.

Glyoxylic acid may likewise be compared with various other bodies; it has, for instance, in many respects a resemblance to sulphurous acid.

Kekulé's interesting experiments with fumaric and maleic acids induced me to examine the action of bromine on a solution of glyoxylic acid. If the two bodies be left in contact at ordinary temperatures in a closed vessel, the colour of the bromine disappears in the course of a few days. Only hydrobromic and oxalic acids, however, resulted from this reaction.

If a rational formula be required for glyoxylic acid, the following expression may be adapted.

$$C_2O\left.\begin{matrix}H\\H\end{matrix}\right\}O_2.$$

It indicates the diatomic nature of the acid as well as its intermediate position between glycollic and oxalic acids. Two atoms of hydrogen added to the radical C_2O produce the radical of glycollic acid, and one atom of oxygen the corresponding radical of oxalic acid.

XXX.—*On the presence of Manganese in Oolite and Lias.*

By Robert Warington, Junr., Assistant to Professor of Chemistry, Royal Agricultural College, Cirencester.

Attention was first called by an accident to the presence of manganese in oolite, a deposit of manganic oxide having been observed during the analysis of a limestone from the neighbourhood of Cirencester. A further hint was received in the course of other experiments. A specimen of Forest marble had been fused with nitre and carbonate of potassium; the mass when exhausted with cold water, gave a solution, having the beautiful sea-green tint of manganate of potassium. In consequence of these suggestions, an examination was made as to the amount of manganese present in some of the strata of the neighbourhood; the analysis was conducted as follows:—

The powdered rock was digested in hydrochloric acid; the solution filtered, peroxidised with nitric acid, and evaporated to dryness; the mass dissolved in water; the solution precipitated in

the cold with carbonate of barium; the filtrate faintly acidified with acetic acid; acetate of sodium and chlorine-water added; and the whole allowed to stand some hours in a warm place. The precipitated binoxide of manganese was then washed with warm water, collected, converted by ignition into Mn_3O_4, and then weighed.

This was found to be, on the whole, a simple and satisfactory method; the only difficulty experienced was in sufficiently washing the oxide of manganese. In the first determinations made, barium was distinctly found on redissolving the precipitate after ignition; but by washing for a longer time, and by adding a small quantity of acetic acid to the wash-water, the amount of barium was easily reduced to a scarcely perceptible trace. In the latest determination, the barium was removed by sulphuric acid before the precipitation of the manganese: these analyses are distinguished by an asterisk.

The specimens analysed, and the results obtained, were as follow:—The manganese is in all cases calculated as manganous oxide, the presence of more or less ferrous oxide in the rocks examined suggesting a low state of oxidation of the manganese.

I. *Kelloway Rock* (Ashton Keynes). A hard, dark grey sandstone.
90·02 grains yielded ·09 grain Mn_3O_4, or ·093 % MnO.

II. *Cornbrash.* A crystalline limestone, very hard, and full of shelly fragments.
108·4 grs. yielded ·18 gr. Mn_3O_4, or ·154 % MnO.

III. *Forest Marble* (Cirencester). A fine-grained limestone of a delicate grey colour.
97·3 grs. yielded ·08 gr. Mn_3O_4, or ·076 % MnO.

IV. *Great Oolite; highest bed.* (R. A. College.) A light-brown shelly limestone.
76·7 grs. yielded ·11 gr. Mn_3O_4, or ·132 % MnO.

V. *Great Oolite; highest bed.* Same quarry as above; specimen extra soft and ferruginous.
86·82 grs. yielded ·12 gr. Mn_3O_4, or ·128 % MnO.

VI. *Great Oolite* (North Leach). Hard, fine-grained, nearly white; a few minute black grains disseminated throughout.
70·53 grs. yielded ·03 gr. Mn_3O_4, or ·039 % MnO.

VII. *Great Oolite* (Bath). A specimen of building stone; cream-coloured, highly oolitic, friable.
62·35 grs. yielded ·06 gr. Mn_3O_4, or ·089 % MnO.

VIII. *Inferior Oolite* (Birdlip). Highly oolitic, hard, nearly white.
103·51 grs. yielded ·03 gr. Mn_3O_4, or ·026 % MnO.

IX. *Inferior Oolite.* Texture very coarse, many black grains disseminated throughout; very ferruginous.
67·45 grs. yielded ·08 gr. Mn_3O_4, or ·109 % MnO.

X. *Cephalopod bed* (Frocester). A coarse ferruginous limestone, of very variable degrees of coherence.
92·29 grs. yielded ·11 gr. Mn_3O_4, or ·112 % MnO.

XI. *Sandy bed, on top of Lias* (Frocester). A soft, calcareous sandstone, varying in colour from brown to grey.
94·14 grs. yielded ·13 gr. Mn_3O_4, or ·128 % MnO.

XII. *Lias; highest bed* (Frocester). A fine-grained argillaceous limestone; light brownish grey.
88·9 grs. yielded ·33 gr. Mn_3O_4, or ·341 % MnO.

XIII. *Lias, shale above marlstone.* A soft grey shale, containing a good deal of pyrites.
* 76·97 grs. yielded ·05 gr. Mn_3O_4, or ·060 % MnO.

XIV. *Lias marlstone.* A calcareous, light-brown sandstone; very ferruginous.
* 99·89 grs. yielded ·34 gr. Mn_3O_4, or ·316 % MnO.

XV. *Lias, bone bed.* A fine-grained argillaceous limestone.
77·47 grs. yielded ·43 gr. Mn_3O_4, or ·516 % MnO.

XVI. *Lias, lowest beds* (Aust Cliff). A hard, blackish limestone, containing veins of calcite, and some pyrites.
78·77 grs. yielded ·22 gr. Mn_3O_4, or ·260 % MnO.
49·71 grs. „ ·13 gr. „ ·243 % MnO.

The following table will exhibit more clearly the proportion of manganese found in the different strata:—

Description of rock.	Percentage of manganous oxide.
I. Kelloway rock	·093
II. Cornbrash	·154
III. Forest marble	·076
IV. Great Oolite (highest bed)	·132
V. „ „	·128
VI. „	·039
VII. „	·089
VIII. Inferior Oolite	·026
IX. „	·109
X. Cephalopod bed	·112
XI. Sandy bed, on top of Lias	·128
XII. Lias (highest bed)	·341
XIII. Lias, shale above marlstone	·060
XIV. Lias marlstone	·316
XV. Lias, bone bed	·516
XVI. Lias (lowest bed)	·251

It will be seen that the percentage of manganese is in every case but small; in the oolitic series this is especially the case, since here it rarely exceeds 1-10th per cent. It was at first thought probable that manganese might be found in larger quantity in some particular situations; and, with this idea, the dark-brown stains frequently found on the vertical joints of the oolite, and sometimes attaining an appreciable thickness, were repeatedly subjected to examination; some oolitic fossils were also analysed; in no instance, however, was a larger amount of manganese found than was known to occur in the rock from which the specimen was taken.

When we turn to the lias, we find that the amount of manganese is considerably above that in the oolite, reaching in some beds to 3-10ths or even 5-10ths per cent. The relative richness of the different beds can, however, scarcely be determined from the scanty information here given. In some of the laminated beds of the lias, dendritic markings occur very extensively; these when examined qualitatively, were found to be rich in manganese.

It remains to be asked, have these small amounts of manganese an appreciable effect upon the organic life of their locality? Professor Church called my attention to the results obtained by Wittstein* in an investigation on this subject. He found the ash of beech-leaves, grown on a soil derived from gneiss, to

* Jahresbericht, 1862.

contain 1·609 per cent. Mn_3O_4; and the ash of the wood, 1·568; the soil in this instance contained 1·410 per cent.

Again with the common birch, growing on a soil containing ·859 per cent. Mn_3O_4, he found the ash of the leaves to yield 5·925 per cent.; and that of the wood, 2·949 per cent. of Mn_3O_4. Other experimenters have obtained similar results.

To ascertain whether the small amounts of manganese present in the oolite would be found accumulated in the vegetation on its surface, a quantity of beech-leaves were gathered towards the end of November from off the lower branches of some young trees, growing on a very shallow soil. 51·74 grs. of the ash yielded ·10 grs. Mn_3O_4, or ·193 per cent.; the rock (great oolite) on which the trees stood, yielded from 132·1 grs., ·05 grs. Mn_3O_4, or ·038 per cent.

More striking results would doubtless have been obtained if the manganiferous soils of the lias had been the subject of the experiment.

XXXI.—*Table for the Calculation of direct Nitrogen Determinations.*

By Jas. T. Brown.

In quantitative analysis, the chemist is anxious to know the result as soon as possible after the completion of his experiments, provided that speed be not attained at the expense of accuracy. Few chemical experiments (gas-analysis and vapour-density determinations excepted) involve more tedious calculations than the determination of nitrogen by Dumas' method. This has evidently been felt: for in the first volume of Gerhardt's "Traité" * there is a small table indicating approximately the values of the expression $760\ (1+0{\cdot}00367\ T)$ for all values of T from 1 to 30. In Bunsen's "Gasometry" † there is another table which can be used for direct nitrogen determinations, viz., one indicating the values of $1+0{\cdot}00366\ T$ for every 0·1 when T is between $-2+40$. But a better table than either is one calculated by Mr. Greville

* Gerhardt, Traité de Chimie Organique, vol. i, page 50.

† Bunsen's Gasometry, translated by Roscoe, page 268.

Williams, to whom I am indebted for a copy, giving the values of $\frac{1}{1+0{\cdot}00367\,T}$ for all the values of T from 1 to 150, and, therefore, applicable also to vapour-densities. From this table I calculated a fuller one of the same range, indicating the values of the expression $\frac{1}{(1+0{\cdot}00367\,T)760}$. From this last table I then advanced to the more comprehensive one which is the subject of the present note, and which indicates the values of $\frac{0{\cdot}0012562}{(1+0{\cdot}00367\,T)760}$ for all values of T from 0 to 30. After I had determined a few terms by this method, I found it necessary, in order to attain the standard of accuracy which I had laid down for myself, to recalculate my values to a greater number of decimal places. In effect, the table which follows, having been calculated to eleven places of decimals, is sufficiently accurate for even the most refined researches which are probably ever likely to be undertaken in the laboratory. This will be seen when I state, that, supposing the gas even to weigh 10 grammes (a quantity far greater than is probably ever weighed, except in physical researches of the highest class), the error of calculation from the use of the table would not amount to a decimilligramme (0·0001 gramme).

In order to find the weight in grammes of any volume of nitrogen at any pressure and temperature up to 30° C., it is only necessary to multiply the number contained in the following table corresponding to the temperature, by the volume expressed in cubic centimetres, and also by the pressure (corrected for tension of aqueous vapour, &c.) expressed in millimetres. I have introduced into the formula for my table all the constant quantities that occur in a direct nitrogen calculation, and one variable, viz., T; so that, by using this table, the calculation is reduced from three multiplications and one long division to two multiplications, as will be seen in the following example. To find the weight of 53 c.c. of nitrogen at a temperature of 15° C., and at a pressure of 743·3 m.m., we have :—

$$0{\cdot}00000156665 \times 53 \times 743{\cdot}3 = 0{\cdot}061718 \text{ gramme.}$$

The chemist must use his own discretion with reference to the number of decimal places to which he uses the table.

I hope, before long, to have the honour of submitting to the Society a table by which vapour-densities can be calculated with

extreme accuracy from the results of experiments, by a process equally simple to that which I have indicated for direct nitrogen determinations.

Table for the calculation of $\frac{0{\cdot}0012562}{(1 + 0{\cdot}00367T)760}$.

T.		T.	
0	0·00000165289	16	0·00000156121
1	0·00000164685	17	0·00000155582
2	0·00000164085	18	0·00000155047
3	0·00000163489	19	0·00000154515
4	0·00000162898	20	0·00000153986
5	0·00000162311	21	0·00000153462
6	0·00000161728	22	0·00000152941
7	0·00000161149	23	0·00000152423
8	0·00000160574	24	0·00000151909
9	0·00000160004	25	0·00000151398
10	0 00000159438	26	0·00000150891
11	0·00000158875	27	0·00000150387
12	0·00000158317	28	0·00000149887
13	0·00000157762	29	0·00000149389
14	0·00000157211	30	0·00000148896
15	0·00000156665		

XXXII.—*Notes on a Cornish Mineral of the Atacamite Group.*

By A. H. Church.

The atacamite from Copiapo, Chili, has invariably, according to Field, the composition represented by the expression—

$$CuCl_2.3CuH_2O_2.aq.$$

In a paper on the cupric oxychlorides of Cornwall, lately published in the "Journal of the Chemical Society," I have shown that the atacamite lately detected in Great Britain, has exactly the same composition, but that it is sometimes accompanied by an uncrystallized blue oxychloride which gives on analysis numbers leading to the formula—

$$CuCl_2.4CuH_2O_2.4\ aq.$$

Mr. Talling has directed my attention to another copper mineral. The quantity as yet found of the last-named substance is small, and my examination of it has been but imperfect. I have, how-

ever, obtained evidence more than sufficient to prove it distinct from the ordinary atacamite. Berthier's atacamite from Tocopilla, Cobija, in Bolivia, the variety *C* of Rammelsberg if the specimen analysed were really pure, may be identical with the present mineral. I give below a condensed account of the composition, &c., of this cupric oxychloride, the third member of the atacamite group occurring in Cornwall.

Botallackite. Usually in thin crusts of minute interlacing crystals closely investing killas. Density near 3·6. Lustre, various. Colour, pale mountain-green. Streak, white. Translucent under the microscope. Composition, $CuCl_2 . 3CuH_2 . O_2 3aq$. The numbers demanded by this formula and those furnished by analysis are :—

Theory ..	Cl 14·76 ..	CuO 66·11 ..	H_2O 22·45	= 103·32
Experiment	Cl 14·51 ..	CuO 66·25 ..	H_2O 22·60	= 103·36

Before the blowpipe and with acids and ammonia, botallackite behaves like atacamite.

Botallackite occurs in a part of the Botallack mine, where an infiltration of sea-water occurs; it is associated with atacamite and tallingite. It seems sufficiently definite to require a name, whether it be ranked as a species, a sub-species, or a variety only.

In the paper before referred to I mentioned the probable existence of a cupric oxychloride (of a darker blue colour), more basic than tallingite. I have obtained fresh supplies of the mineral, and the analyses gave the following numbers :—

·349	gramme of substance	gave	·1205	grm. AgCl
·593	„	„	·211	„
·593	„	„	·4	„ CuO
·349	„	„	·234	„ „
·593	„	„	·1575	„ H_2O

The mean percentages deduced from these numbers and compared with those demanded by the formula $CuCl_2.6CuH_2O_2.6aq$. are as follows :—

	Experiment.	Theory.
CuO	67·25	67·25
Cl	8·73	8·58
H_2O	26·56	26·13

But as other analyses gave numbers less accordant with the above

formula, I am not inclined to acknowledge without hesitation the existence of another blue oxychloride.

The native oxychlorides of copper may be divided into two groups, as shewn in the annexed list :—

GREEN OXYCHLORIDES.

Atacamite Group.

Atacamite	$CuCl_2.3CuH_2O_2.aq$
„ var. *A* of Ramm^s	$CuCl_2.3CuH_2O_2$
„ var. Botallackite	$CuCl_2.3CuH_2O_2.3aq.$

BLUE OXYCHLORIDES.

Tallingite Group.

Tallingite	$CuCl_2.4CuH_2O_2.4Aq.$
„ var.?	$CuCl_2.6CuH_2O_2.6aq.$

How far these minerals are transitional states of others—whether in fact they are all perfect or *mature* minerals—synthetical experiments may aid in determining. The action, for example, of sea-water or, better, of a 10 per cent. solution of NaCl, on chessylite, or malachite, promises interesting results.

XXXIII.—*Notes on a Ferric Hydrate from Cornwall.*

By A. H. CHURCH.

IT is rare to find a specimen of limonite to which a definite formula can be attached, while even the carefully prepared artificial salt is very variable in its composition. Under these circumstances an analysis of a well-formed stalactite of limonite from the Botallack mine may prove of interest. The stalactite, which contained an unusually small proportion of phosphoric acid, weighed about 4 grammes, and was of a pure and uniform rust colour, slightly subtranslucent in part, and having a smooth bright surface. Its density was 2·69. Freed from hygroscopic water, it yielded the following results on analysis :—

5·96 grains gave

2·601	grains	Fe by permanganate method;
·42	„	SiO_2;
1·33	„	H_2O;
·31	„	NaCl and other soluble salts;
·19	„	other substances.

Calculating the iron and water found into percentages, after deduction of the silica, common salt, and other evident impurities, we arrive at the following numbers:—

	Experiment.	Theory, $Fe'''H_3O_3$.
Ferric oxide	73·73	74·77
Water	24·40	25·23
Loss, &c.	1·87	
	100·00	100·00

The loss includes the undetermined phosphoric acid and organic matter. The total amount of loss on ignition was ascertained in a special experiment to be 25·49 per cent.

It will be seen that this specimen of limonite was the normal ferric hydrate $Fe'''H_3O_3$ or $Fe'''(HO)_3$.

XXXIV.—*Analyses of some Bronzes found in Great Britain.*

By A. H. Church.

During the progress of the Main Drainage works, a large number of small articles of bronze have been discovered. Antiquarians entertain no doubt of the authenticity of a certain portion of these specimens of Roman-British manufacture. Last year Mr. R. H. Soden-Smith placed in my hands for analysis two bronze needles found in 1864, at Southwark. One of these was quite untarnished when the earth was washed off it, and presented a most beautiful and rich gold colour. On analysis it gave the following results:—

Copper	84·27	per cent.
Zinc, with a little iron	14·70	„
Tin	2·36	„
	101·33	

The excess over the 100 parts is probably in part due to the presence of ferric oxide in the substance weighed as zinc-oxide, the larger percentage of oxygen in the former compound rendering the calculation inexact.

Another specimen less beautiful in colour had the following composition:—

Copper	84·90	per cent.
Zinc, with a little iron	13·00	„
Tin	1·03	„
Lead and impurities	1·07	„
	100·00	

These analyses (and others already published) show that much of the so-called bronze of the Roman period found in Britain should, correctly speaking, be termed brass. In the ethnological gallery of the British Museum, however, the word bronze is still retained for specimens exactly resembling those which I have analysed and obtained from the same locality.

A comparison of Celtic bronzes with those of Roman-British origin, just described, offers some considerations of interest.

At Aboyne, not long since, three massive bronze armlets were found. The workmanship and design seem to prove them to belong to the period anterior to the Roman possession of Britain. A very small fragment of the metal was taken from these rare and interesting specimens, by permission of their owner, the Marchioness of Huntly, and handed to me for analysis by Mr. Soden-Smith.

	Armlet No. 1.	Armlet No. 2.
Copper.....	86·49	88·19
Tin	6·76	3·64
Zinc.....	1·44	9·13
Lead.....	4·41	—
Loss and oxygen, &c...	·90	—
	100·00	100·96

The injurious effects of lead upon brass and bronze are well known. In the present case (of armlet No. 1) there was marked evidence of a deterioration in the alloy, produced by the large proportion of lead present,—for the armlet, though very massive, had been

broken (and mended) at the period of its use. The metal was cracked, the fissures presenting the appearance of some lead-containing bronzes after they have been worked when hot.

XXXV.—*The estimation of Indigotin, or the blue colouring matter of Indigo.*

By Clemens Ullgren.

In estimating a few years ago the value of a certain sort of indigo, I made use both of the so-called method of reduction, and of the methods which tend to change indigotin by oxidation, in such a manner, that the blue colour disappears, and *can no more be restored.* It appeared, however, that the results of the first-mentioned method, compared with those of the latter ones, or the so-called methods of volumetric analysis, always differed greatly from each other. Berzelius, in the description of his method* of estimating the blue colouring matter by chlorine, has certainly mentioned that the quantity of the former obtained in this way is always a little greater than the reality, in consequence of the influence of the chlorine on other organic matters with which the indigotin in the indigo is accompanied; he, however, assumed that the error thence arising could not be very great, and the same has also been assumed by others, who have since published methods for estimating the quantity of colouring matter by titration. In my experiments, however, I found, as before mentioned, that the error in question is by no means insignificant, and moreover varies so much according to the degree of dilution, as well of the solution of indigo as of the standard solution, that with the same sort of indigo, by using the method of volumetric analysis, with permanganate of potassium, for instance, I obtained from 34 to 80 % more indigotin than was found by reduction. Seeing now that so many millions of pounds of indigo are yearly consumed (according to Girardin, nearly ten millions of pounds were exported from the several places of manufacture during a single year), and that the quality in the different sorts may vary considerably, without any corresponding difference of external appearance,

* Berzelius, *Lehrbuch der Chemie*, Bd. VII, 3te Auflage, pag. 242.

an easily performed, but also tolerably sure method of estimating the real quantity of the colouring matter must be considered of importance. I have therefore endeavoured to find such a method, and shall here describe some of my experiments, in the form of answers to certain anticipated questions.

1. *Will the same results be obtained if the reduction of indigotin is performed by a solution of grape-sugar in alcohol with hydrate of sodium (Fritsche's method), or by a solution of ferrous sulphate with hydrate of sodium?*

a. 0·56 grm. Bengal indigo No. 1, dried at 110°, was digested with a solution of 3 grms. hydrate of sodium in 10 c.c. of water, and so much saturated solution of grape-sugar in alcohol of 76 %, that the whole amounted to 100 c.c.—50 c.c. of this returned 0·172 grm. indigotin, dried at 100°: consequently there was in 100 c.c 0·344 grm. = 61·43 %.

b. 0·35 grm. of the same sort of indigo, dried at 100°, was digested with a solution of 3 grms. sodic hydrate and 1 grm. ferrous sulphate ($FeSO_4 . 7HO$), in so much water that the whole amounted to 100° c.c.; 50 c.c. of this returned 0·1085 grm. indigotin dried at 110°; consequently the whole value of the indigotin, 0·217 grm. = 62 %.* The two experiments gave, therefore, very nearly the same quantity of indigotin.

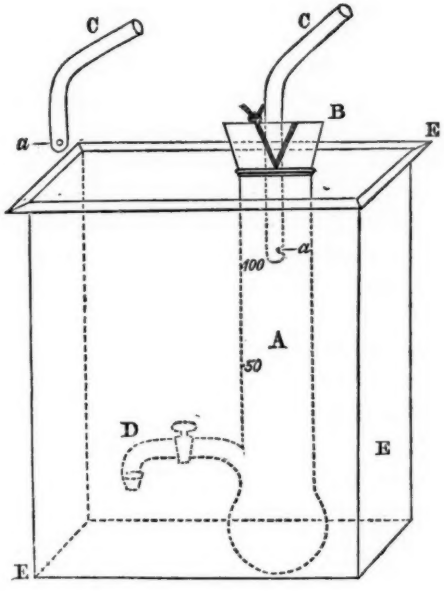
The filters in these, as well as in the reduction experiments hereafter described, were washed, before drying and weighing between watch-glasses, with double the quantity of hydrate of sodium dissolved in 100 c.c. water, as was afterwards used for the reduction, in order to drive out of the paper all that the soda was able to dissolve. In separately made experiments, the difference before and after the washing with soda-solution was no greater than 3—5 milligrammes for a filter weighing 3 to 4 decigrammes.

The apparatus I used in the reduction experiments was constructed as shown by the annexed figure.

It consists of a tube *A*, closed at one end, 3 centimetres in diameter and 24 centimetres in length; the other end is closed by an India-rubber stopper, *B*, through which the smaller tube, *C*, can be drawn up and down, the lower end of this being also closed up, but with a small opening, *a*, just above the end. If this tube is drawn upwards so much, that the opening, *a*, is within the hole of the India-rubber stopper, and there tightly enclosed,

* In two experiments where lime was used, only 53 and 57 °/₀ of indigotin was obtained. As an error may arise from the difficulty of dissolving the compound of indigotin and lime, I used soda instead of lime in the subsequent experiments.

the whole apparatus will become perfectly air-tight. This tube cannot well be replaced by a tube opening inwards, and closed externally by a cock or spring-clamp, because when shaken the contents of the wider tube would always enter it. The tube *A* is also provided with a cock-tube, *D*, bent inwards, through which the liquid can be drawn off, and also with a mark showing the cubic measure of 100 c.c. In the digestion, it is heated to 80° or 90° in the water-bath, *E*, over a gas-flame. The stopper should, before the warming up, be tied down with a piece of cord, as shown in the figure.



With this apparatus, no more than a few decigrammes of the sample of indigo need be used, whereby the experiment is greatly facilitated. When sulphate of iron is used, I find it best, as Mohr prescribes, with indigo dissolved in sulphuric acid, to put into the reduction-tube 10—15 grms. of small garnets, by which the indigo-powder, which in finer sorts of indigo floats for a long time on the top of the liquid, is more easily brought in contact with the ferrous hydrate by agitation. By frequent shaking during the digestion, the blue colouring matter is very soon dissolved, and when grape-sugar is used, we may ascertain by the appearance

of the undissolved matter, when the reduction is finished, which takes no more than a couple of hours. The apparatus is then taken out of the water-bath, and hung up in a convenient position. When the liquid has become perfectly clear and cool, the interior of the apparatus must be placed in connection with the outer air, by depressing the tube *C*, after which 50 cc. are drawn off into a small glass bulb, which contains just that quantity when filled to a certain mark in the narrow neck. Dumas, as is well known, determined the now-adopted atomic constitution of indigotin and indigo-white, and in respect to the origin of the latter, he proved that it is due, not to the reduction* of indigotin, but to the combination of the latter with 1 equivalent of hydrogen. This opinion was afterwards adopted by Berzelius, although he at first differed from it; because in determining the quantity of copper that indigo-white reduces from a cupric salt, in its reconversion into indigotin, he obtained far less copper than he ought to have had, according to the formula given by Dumas†. Considering the accuracy by which all the analytical works of the great master are characterised, it occurred to me that the considerable loss of copper in his experiments, about 25 %, must have had some hidden cause, and could not be due to mere chance. Hence I was led to the following question :—

2. *If pure indigotin is subjected to "reduction," can the original quantity of indigotin be re-obtained?*

0·527 grm. indigotin dried at 110°, was digested in the before-mentioned apparatus, with 3 grms. hydrate of sodium in 10 c.c. water, and so much of a saturated solution of grape-sugar in alcohol of 76 %, that the whole amounted to 100 c.c. A clear red-brown liquid was thus obtained, 50 c.c. of which yielded 0·2289 grm. indigotin; 100 c.c. should therefore yield 0·4578 grm., which is equal to only 86·87 per cent. of the quantity used for the experiment.

Part of the indigotin was therefore changed to something different from indigo-white, and this part is here equal to 13·13 per cent.

The indigotin used in this experiment was prepared from Bengal indigo, with sulphate of iron and lime, and afterwards twice reduced by Fritsche's method.

* For facility of expression I have, in this paper, kept this term for the change of indigotin into indigo-white.

† Berzelius, *Lehrbuch der Chemie*, Bd. VII, 3te Auflage, S. 235.

3. *Does an increase of the quantity of hydrate of sodium, within certain limits, contribute towards the destruction of indigotin in this reaction?*

0·21 grm. indigotin of the kind that had been oxidised in previous experiments, was treated with 5 grms. hydrate of sodium, consequently more than four times the quantity of hydrate of sodium used in the previous experiment, and a solution of grape-sugar equal to the one in the last experiment; 50 c.c. of this yielded 0·092 grm. indigotin; or in 100 c.c. there was 0·184 grm., or 87·62 % of the indigotin employed, and consequently 0·75 % more than when only a one-fourth the quantity of hydrate of sodium was used.

4. *Is the destruction of indigotin a consequence of the manner in which the grape-sugar is decomposed in this reduction, or is it independent thereof, and does it likewise happen when a proto-salt of iron is used instead of grape-sugar?**

0·1955 grm. indigotin (from the very last experiment), dried at 110°, was treated with 3 grms. hydrate of sodium and 1 grm. ferrous sulphate ($FeSO_4 . 7HO$), and water to the measure of 100 c.c.;—50 c.c. of this yielded 0·085 grm. indigotin. Consequently 100 c.c. yielded 0·17 grm., equal to 87 %, or a loss of 13 % of the indigotin used, or, as is seen, the same quantity as when grape-sugar was used.

According to Dumas' formula for indigo-white, the conversion of 100 pts. of the latter into indigotin by oxidation, at the expense of copper-oxide, will reduce 24·8 pts. copper, that is to say, *if no part of the indigotin has been destroyed in changing it to indigo-white.* There is, however, according to what I before have shown, in round numbers 13 % indigotin destroyed; therefore the quantity of copper that should be reduced is only 21·03 %. Berzelius obtained 18·35 %.† The reason is now clear, why he obtained less copper than the formula for indigotin shows, even if it still remains to be discovered why the loss was nearly twice as great as what was caused by the lost 13 % of indigotin. I intend, however, to pursue the experiments concerning this as well as other circumstances connected with the results here obtained.

Although the method of reduction is very easily carried out with

* The answer may certainly be drawn from the test No. 1, but will not be fully ascertained until obtained from a result based upon *pure* indigotin free from other organic matters.

† Berzelius, *Lehrbuch der Chemie*, Bd. VII, 3te Auflage, pag. 235.

the apparatus above described, it requires the greatest accuracy, and too much practice in the more refined operations of analysis, to be practical, especially if many samples of indigo are to be valued at the same time. The methods of volumetric analysis are therefore to be preferred. In applying them, however, it is necessary to dissolve the indigo in concentrated sulphuric acid; but in the acid solution thus obtained there are two principal sources of error, the one being due to the presence of indigo-gluten, indigo-brown, and indigo-red, as before mentioned, the other to protoxide of iron, from the ashes of the indigo, which also consumes part of the standard solution for its oxidation. In the finer sort of indigo the amount of ash is certainly very small, often not amounting to 1 %; but I have met with indigo, Madras No. 3 for example, which left 72 % of ash of a red-brown colour, and consequently containing a larger quantity of iron-oxide.

This source of error may be avoided by making the volumetric analysis in an alkaline instead of an acid solution. After many unsuccessful experiments, the description of which I here pass by, to obtain by the method of volumetric analysis, results corresponding, at least in some degree, with those of the method of reduction obtained at the same time, I at last found in ferricyanide of potassium a means of attaining my object.

It has long been known that ferricyanide of potassium, in presence of free alkali, destroys the colour of indigotin, and changes the colouring matter, as is supposed, to isatin, thus:—

$$C_{16}H_5NO_2 + 2K_3Fe_2Cy_6 + 2KO = \underset{\text{Isatin.}}{C_{16}H_5NO_4} + 4K_2FeCy_3$$

That however the reaction can take place in many other ways is seen by the different *quantity* of the ferricyanide required, if a greater or lesser excess of the caustic potash is used, to which a difference of 8—10 degrees in temperature also contributes.

This circumstance renders it difficult to obtain corresponding results. But the case is altered when, instead of caustic alkali (oxide of sodium, for example), carbonate of soda is used. Of this, a certain minimum is required to render the results constant, but above this minimum, the quantity of carbonate of soda may afterwards be very considerably increased, without any very perceptible influence, if only the following particulars are observed:—

1. The quantity of sulphuric acid added to the solution of indigo should not be too great, and the temperature must not exceed 50°, because, especially with impurer sorts of indigo, sulphurous acid in considerable quantity is then generated, and combinations with sulphuric acid are obtained, part of which are not dissolved in the acid liquid when diluted with water, like sulphopurpuric acid.

In experiments to dissolve, along with the indigo, separately added quantities of indigo-gluten, indigo-brown, and indigo-red, in order to ascertain their influence on the certainty of the method,—the quantity of sulphuric acid used being fifteen times the weight of the indigo, and the temperature not exceeding 50°, only a yellow solution was obtained on two different occasions after diluting with water; and when the blue substance on the filter was washed, it was certainly dissolved in the same proportion as the free acid was removed, *but very* slowly. The quantity of sulphuric acid that I have found most suitable is ten times the weight of the indigotin and eight times that of the indigo, the acid itself being of the strength which *is obtained when fuming sulphuric acid is mixed with distilled water until the mixture only is faintly fuming.* With this strength of acid the formation of a certain portion of sulphopurpuric acid is of less consequence; only in measuring for titration the diluted liquid must be well shaken.

2. *The indigo solution should be very much diluted,* and a sample preserved in order to serve as a guide as to the degree of dilution. To prepare the standard solution, 1 gramme of pure indigotin is dissolved in 10 grammes of sulphuric acid, mixed with water to 1 litre of liquid, and 10 c.c. of the solution thus obtained is also diluted to 1 litre of liquid; in this there are, consequently, 10 milligrammes of indigotin dissolved. The solution of indigotin to be tested should be so much diluted that it may be lighter than this sample-coloured solution.

3. *The solution of carbonate of soda* should be saturated in the cold. 20 c.c. of this solution is mixed with the quantity of indigo solution which has been measured and afterwards diluted to be titrated; it is so proportioned that its value of indigotin is about 10 milligrammes, but rather below than above this quantity.

4. *The solution of ferricyanide of potassium* should also be very dilute. If 5·023 grms. of this salt is dissolved in 1 litre of water, then, with a certain quantity of oxide of sodium, 1 c.c. of this solution destroys 1 milligramme of indigotin. But if carbonate of soda is used in corresponding quantity, another reaction takes

place, in consequence of which nearly a double quantity of ferricyanide of potassium is required. This, however, is of no consequence in practice, provided we know *how much* of a solution of ferricyanide of potassium of given strength is required to destroy 1 milligramme of indigotin in solution, rendered alkaline by carbonate of soda. The solution of ferricyanide of potassium used in my experiments contained 2·5115 grms. of that salt in a litre, consequently 2 c.c. of it would just have changed 1 milligramme of indigotin into isatin.

5. When carbonate of soda is used, and the liquid is diluted to the degree of dilution above-mentioned, *the change of colour* is shown in such a way that the blue colour gradually disappears, without distinctly changing into green, as is the case when the dilution is less. When the liquid has assumed a grey-yellow appearance, or generally when every tint of blue has disappeared, the operation may be regarded as complete.

The titration should be done slowly and with frequent stirring by a glass rod, and this is most easily done if the liquid is poured into a large porcelain basin, where also the change of colour can be most distinctly observed.

As an example of the applicability of the method, I will here describe a few results:—1 grm. pure indigotin was dissolved in 10 grms. of sulphuric acid, and the solution was diluted to 1 litre; 10 c.c. of this mixed in a porcelain vessel, with 1 litre of water and 20 c.c. of a cold saturated solution of carbonate of soda, required, at a temperature of 18°, in four experiments, of the solution of ferricyanide of potassium: 34·5, 35·35, 35·5 c.c.: mean 35c.c.

1 grm. Bengal indigo, No. 1, which in the reduction, partly with grape-sugar, partly with sulphate of iron and soda, was found to yield in even numbers 62% of indigotin, was dissolved in 8 grms. of sulphuric acid, and diluted with water to 1 litre; 10 c.c. of this mixed with $\frac{3}{4}$ litre of water and 20 c.c. of a solution of oxide of sodium saturated in the cold, required at a temperature of 18°, in four experiments, 23, 22; 22·5 and 23 c.c. of the solution of ferricyanide of potassium: mean 22·6 c.c. But 35: 22·6 = 100: $x = 6\frac{1}{4}$% indigotin, consequently 2·4% more than was shown by reduction.

Similar approximate results, with 2 to 4% excess over those from the method of reduction, were obtained in experiments with several other kinds of indigo.

The preceding results may be thus summed up:—

1. By the so-called reduction of indigotin, the same quantity of colouring matter is restored, whether sulphate of iron or grape-sugar is used ; but

2. Of the indigotin employed, only *a part will be recovered,* making about, according to my experiments, 87 %. The addition of hydrate of soda, *within certain limits,* makes no difference on the result.

3. To ascertain the amount of indigotin in the original samples, a quantity corresponding with the loss of 13 % must be added to that found by weighing. The quantity found directly is, on the contrary, that which can be made use of in the indigo-vats, because in dyeing with indigo, the same kinds of reduction-methods as those here used cause the same loss of colouring matter.

4. With ferricyanide of potassium in the proportions above-mentioned, the quantity of indigotin in certain sorts of indigo may be approximatively estimated with an error of only a few %, while in all the hitherto described methods of volumetric analysis, the error may amount to 80 %.

5. Since the quantity of indigotin found by this method is equal or nearly equal to that obtained from the very same sort of indigo by the method of reduction, it seems likely that one part of indigotin dissolved in sulphuric acid is altered in a manner different from the rest.

Appendix.

Since the above was communicated to the Royal Academy of Sciences, I have found in the "Journal für praktische Chemie," published the 7th of last October, 1864, a communication by Professor Erdmann, who has also directed attention to the uncertainty of the hitherto known methods of volumetric analysis for estimating the colouring matter of indigo. His experiments corroborate my statements concerning the difference in the results obtained when using the method of reduction and several published methods of volumetric analysis. By experimenting with two different kinds of indigo, he obtained from 70 to 90 more with the latter than with the former.

XXXVI.—*On the Qualitative Analysis of Substances Insoluble in Water and Acids.*

By Charles L. Bloxam.

In the ordinary course of qualitative analysis, the insoluble residue after treatment with water and acids, is fused, either with carbonate of soda alone, or with the more easily fusible mixture of carbonates of potash and soda. The fusion is generally effected in a platinum crucible or on platinum foil, and often requires a prolonged application of the blowpipe flame. It is necessary also to submit the substance to a preliminary examination for the easily reducible metals which would corrode the platinum. When such metals are present, a porcelain crucible is employed, when the fused mass becomes contaminated with silica and alumina derived from the crucible, which is often so far corroded as to be useless. With an ordinary gas-burner and blowpipe it is not easy to raise the porcelain crucible to the high temperature required for the fusion.

A great saving of time and labour may be effected by causing the heat to be applied *inside* the mass to be fused. For this purpose it is mixed with charcoal and nitre in such proportions that complete deflagration and consequent fusion will take place on applying a lighted match. The fusion may thus be effected in a thin porcelain dish without the least injury to the glaze. If the dish be uniformly thin it is not cracked by the deflagration, but if such a dish be not at hand, a clean iron sand-tray answers the purpose, the iron being not in the least affected by the deflagrating mixture. The charcoal should, of course, be chosen so as to yield a very small proportion of ash, and must be reduced to a fine powder.* Chemically pure nitre is in common use in the laboratory.

A mixture of one part by weight of charcoal with six parts of nitre forms an excellent "deflagrating flux," and may be kept ready mixed for effecting the fusion of insoluble substances. The fused mass remaining after the deflagration is very porous, and, therefore, easily disintegrated by water, whereas the mass obtained by the ordinary process of fusion by external heat often

* Charcoal from the powder-mills is most suitable for the purpose.

requires digestion with water for an hour or two in order to extract the soluble part.

The following is the process which I have adopted for the rapid examination of insoluble substances :—

5 grains of the substance are intimately mixed with 10 grains of dried carbonate of soda, and 70 grains of the "deflagrating flux."* The mixture is placed in a thin porcelain dish, or clean iron tray, and a lighted match applied to the centre of the heap. The deflagration is completed in two or three seconds, and a well-fused mass remains. This is easily detached from the cooled dish (in which a little unburnt charcoal may be left), and boiled with water, being occasionally stirred with a glass rod. Two or three minutes always suffice for the extraction of the soluble portion, which is then filtered off, and examined as usual for acids and for such bases as are compatible in solution with the alkaline carbonates. The residue left by water, after having been washed, is treated with acids and examined in the usual way. A little charcoal is generally left undissolved by acids, and with it any of the substance which may have escaped decomposition. If it be thought necessary, the dried residue may be ignited until the charcoal is consumed, and the incombustible portion examined.

The only substance which resisted the above mode of treatment was chrome-iron-ore, but this is not surprising, since this mineral is only partially decomposed even by prolonged fusion in the ordinary manner with the alkaline carbonates.

Quartz sand was rendered almost completely soluble by this process, and by using twice the proportion of carbonate of soda it became entirely so.

Pipe-clay was completely fluxed. The aqueous solution of the fused mass contained, of course, very little silica or alumina, which were both found in the gelatinous residue dissolved by hydrochloric acid.

Fluor-spar, one of the most troublesome substances under the ordinary mode of fusion, is almost completely decomposed by the deflagration. The aqueous solution, when neutralized with acetic acid, and mixed with chloride of calcium, gives an abundant precipitate of the characteristic fluoride of calcium.

Heavy-spar is completely decomposed by the deflagration,

* This appears to be a large proportion of the deflagrating mixture, but the greater part of it will of course pass off during the deflagration.

yielding sulphates of the alkalies in the aqueous solution, and a residue of carbonate of baryta perfectly soluble in hydrochloric acid. This might be recommended as a convenient laboratory-process for the preparation of soluble baryta-salts from heavy-spar, since the commonest saltpetre, when dried, would answer the purpose.

Tinstone was also rendered in great measure soluble by this mode of treatment. The aqueous solution contained much stannic and silicic acids, whilst the residue furnished a large quantity of soluble binoxide of tin on treatment with hydrochloric acid.

Flint-glass was very completely decomposed, some of the lead separating in globules during the deflagration. The aqueous solution contained very little lead, and abundance of silica. The portion left by water dissolved in dilute nitric acid, leaving a few particles of charcoal.

Window-glass was also easily analysed in this way.

Felspar was not so completely decomposed, though abundance of silica and alumina could be detected in the hydrochloric solution from the deflagrated mass.

Chloride of silver was, of course, completely decomposed, the silver separating in the metallic state.*

Sulphate of lead was also completely decomposed, with separation of some metallic lead. Alkaline sulphates were found in the aqueous solution.

Kryolite, as might be anticipated, was very easily decomposed, some of the aluminum being found, together with alkaline fluorides, in the aqueous solution, while the rest, as alumina, dissolved in hydrochloric acid.

In cases where it is not desired to examine for sulphates, a mixture of nitre with gunpowder may be very advantageously substituted for the nitre and charcoal. The mixture being more powerful, allows the use of a larger proportion of carbonate of soda, thus ensuring more complete decomposition. One part, by weight, of the insoluble substance may be mixed with four parts of carbonate of soda, four parts of nitre, and ten parts of finely-powdered gunpowder.

I have examined all the above-mentioned substances by this process also with equally satisfactory results.

* This method of treating insoluble substances was originally suggested by Mr. Hadow's process for extracting the silver from old photographic baths by deflagrating the precipitated chloride with saltpetre and wood.

Examination of Insoluble Substances for Alkalies.

The ordinary process of fusion with baryta for the detection of alkalies is attended with some inconvenience. The baryta itself is not a pleasant reagent, nor is it always easy to obtain it free from alkalies. If the fusion be performed in platinum, the metal is slightly attacked; if in porcelain, there is danger of introducing alkali from the glaze which is always affected. The fused mass is generally difficult to detach, and is so slowly attacked by water that it has to be dissolved in hydrochloric acid, which involves the separation of a large quantity of baryta, as well as of magnesia, before seeking for the alkalies. I have found that the use of a mixture of nitrate of baryta and sulphur obviates these difficulties and enables the decomposition to be easily effected by the heat of a spirit-lamp.

Nitrate of baryta is, of course, easily obtained in a pure state, and flowers of sulphur may be depended upon as free from alkalies.

One part, by weight, of the substance under examination is mixed with one part of flowers of sulphur and six parts of nitrate of baryta; the mixture is introduced into a porcelain crucible and quickly heated, over a spirit-lamp or air-gas flame, until the deflagration is over; about one minute suffices for this. The crucible is allowed to cool, the fused mass loosened at the edge with the point of a knife, and thrown into a mortar, where it is easily reduced to a fine powder. (The glaze of the crucible will be found quite untouched.) The powder is thrown into a little boiling water, in a dish, boiled for a minute or two, and filtered. The filtrate is mixed with ammonia and carbonate of ammonia, and boiled, to separate baryta and other alkaline earths which may be present, and after these have been filtered off, the solution is evaporated, and the examination for alkalies conducted in the ordinary manner.

Flint-glass (5 grains) was examined in this way. The potassium was very readily detected. No potassium was found to have been left in that portion of the fused mass which was insoluble in water.

Felspar (5 grains) gave an equally satisfactory result. In this case also, no potassium could be found in the residue left by water.

Window-glass (5 grains) gave the sodium-precipitate very dis-

tinctly with antimoniate of potash, in characteristic strongly adherent crystals. No potassium was detected.

Kryolite (5 grains) also gave antimoniate of soda very distinctly. No indication of potassium.

The economy of time, fuel, and crucibles resulting from the application of the processes above described, will be found, I hope, to justify my belief that they are not undeserving of the attention of a Society which includes a large number of practical chemists.

XXXVII.—*On the Theory of Isomeric Compounds.*

By Dr. A. Crum Brown.

In the following remarks I intend to confine myself to the consideration of those compounds which have not only the same composition per cent., and the same molecular weight, but also the same constitutional formula. Such compounds may be termed absolutely isomeric. As the constitutional formula of few substances is fully known, this class is of course a small one, or rather there are few substances of which we can certainly say that they belong to this class.

The following are the principal pairs of substances which are or have been supposed to be absolutely isomeric. I shall first enumerate them, and then proceed to discuss the nature of their isomerism.

1. The hydrides of the alcohol-radicals, and the so-called alcohol-radicals, as hydride of ethyl and methyl gas; hydride of propyl and methyl-ethyl.
2. Chloride of ethyl and the product of the action of chlorine on hydride of ethyl. Also the chlorides of other alcohol-radicals and the mono-chlorinated derivatives from the corresponding hydrides.
3. Chloride of vinyl and chloracetene.
4. Fumaric and maleic acids.
5. Two of the three acids citraconic, itaconic, and mesaconic.

6. Bromo-maleic and isobromo-maleic acids.
7. Bibromo-succinic and isobibromo-succinic acids.
8. Active and inactive malic acid.
9. Active and inactive aspartic acid.
10. Two of the varieties of tartaric acid.
11. The two series of bodies known as the compounds of ethylene and of ethylidene.
12. Lactic and paralactic acids.
13. The two series of alcohols derived, the one by fermentation from sugar, and the other by the addition of water to the olefines, as Berthelot's and Friedel's propylic alcohol, Wurtz's hydrate of amylene, Erlenmeyer and Wanklyn's β hexylic alcohol.

To the same class belong of course the ethers derived from these alcohols.

14. The isomeric acids and alcohols having the general formula $C_nH_{2(n-3)}O$, as kressylic acid, and benzoic alcohol.

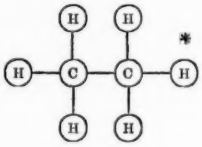
I now proceed to inquire whether these pairs of substances are absolutely isomeric or not.

In order to do so, we must determine whether they are really different, whether they are not perhaps identical; and secondly, whether they are or are not metameric; in other words, whether the theory of atomicity is insufficient alone to explain their difference.

1. Are there two isomeric series having the common formula $C_nH_{2(n+1)}$? Or are these bodies identical? Till lately, most chemists would have replied unhesitatingly that these substances were different. According to the observations of Frankland, hydride of ethyl and methyl gas, otherwise so like one another, show a very different reaction when treated with chlorine in diffused day-light. Were this observation confirmed, it would be quite sufficient to prove that the two bodies were not identical. Several chemists (Carius, Schorlemmer) have, however, lately expressed doubts as to the correctness of Frankland's observation, and it would certainly be satisfactory that it should be repeated with special precautions.

That these bodies are not metameric, that is, that the theory of atomicity is incapable of explaining the difference between them (assuming, as we may do, till Frankland's observation be found incorrect, that there is a difference), is evident. For there is on that theory only one possible constitutional formula for a substance

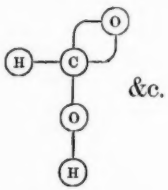
having the composition and molecular weight expressed by the empirical formula C_2H_6, viz. :—



The same reasoning is sufficient to show that the other pairs in this series, as methyl-ethyl and hydride of propyl, ethyl and hydride of butyl, &c., are not metameric. The question of the *identity* of these bodies must, however, be still regarded as an open one.

2. There can be little doubt that chloride of ethyl and the substance produced by the reaction of chlorine on hydride of ethyl are essentially different. The former boils at + 11° C., the latter is a gas not condensable by a cold of −18°C. There is also a great difference between them as to solubility in water. They cannot be metameric, as there are not two possible constitutional formulæ for C_2H_5Cl. They are therefore absolutely isomeric. The same argument does not hold in the case of any of the homologues of chloride of ethyl except chloride of methyl. For there may be two formulæ for the molecule C_3H_7Cl, two for C_4H_9Cl,

* I may here shortly explain the graphic notation which I employ to express constitutional formulæ, and by which, it is scarcely necessary to remark, I do not mean to indicate the physical, but merely the chemical position of the atoms. An atom is represented by its usual symbol, surrounded by a circle with as many lines proceeding from it as the atom contains equivalents, thus an uniequivalent atom is represented by (A)–, a biequivalent atom by –(B)– or (B)=, and so on of the others. When equivalents mutually saturate one another, the two lines representing the equivalents are made continuations of one another, thus water is (H)—(O)—(H). Formic acid

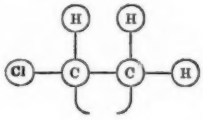


&c.

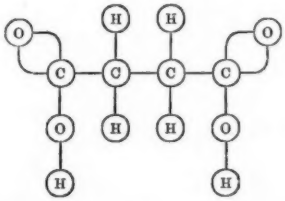
This method seems to me to present advantages over the methods used by Professors Kekulé and Erlenmeyer; and while it is no doubt liable, when not explained, to be mistaken for a representation of the physical position of the atoms, this misunderstanding can easily be prevented.

three for $C_5H_{11}Cl$, &c., without varying the mode of arrangement of the carbon atoms *inter se*.

3. Chloride of vinyl and chloracetene are undoubtedly different. They resemble one another in nothing but composition and molecular weight. If we exclude the possibility of the existence of diatomic carbon* in such a molecule, there is only one constitutional formula to represent them both,

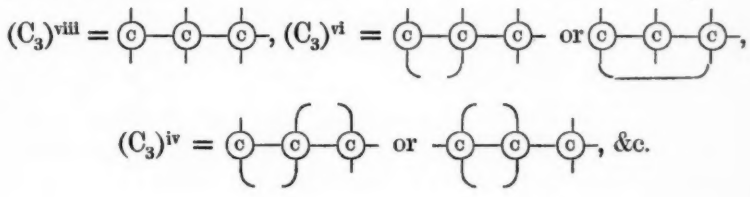


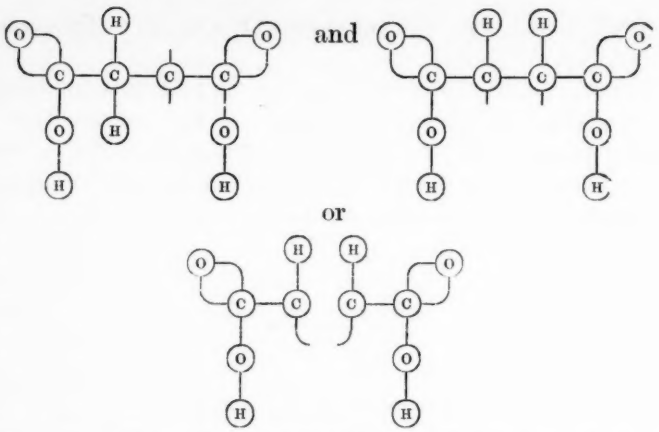
4. The constitutional formula of succinic acid is



Maleic and fumaric acids, each form succinic acid by the addition of two atoms of hydrogen. And as both are dibasic, these two atoms of hydrogen cannot be contained in either of the groups HO in succinic acid. They must, therefore, be two of the hydrogen atoms directly combined with carbon. Now, there are two conceivable constitutional formulæ by which they could be represented—

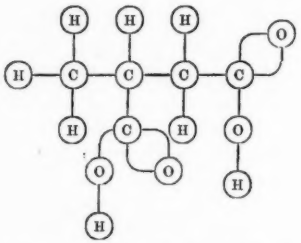
* I do not intend to deny the possibility of this, but all we know of such "non-saturated" substances leads to the belief that the atomicity of the carbon radical C_n is reduced, not by one or more of the carbon atoms becoming diatomic, but by the union of the carbon atoms taking place in the way represented by the following graphic formulæ:





Of these the latter only is admissible, for the theory of atomicity taken strictly does not admit of free affinities in a molecule. This formula then must be common to the two acids.

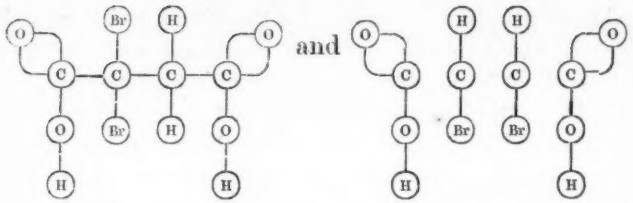
5. In the abstract of this paper, published in the Society's "Proceedings," the dehydrogenates and the bibromo derivatives of pyrotartaric acid were inadvertently included in the list of bodies probably absolutely isomeric. From the relation of pyrotartaric acid to propylene, and of the latter substance to Friedel's alcohol, we may deduce the following formula for pyrotartaric acid :—



If this formula be correct, it is obvious that there *may* be three metameric dehydrogenates and bibromo derivatives.

6. As the two atoms of hydrogen in the radical of maleic acid are, on the theory of atomicity, in precisely similar positions, it is obvious that there cannot be two metameric bromo-maleic acids And as Kekulé has shown that there are two acids, bromo-maleic and isobromo-maleic, these must be absolutely isomeric.

7. Two perfectly admissible formulæ can be constructed to represent bibromo-succinic acid :—



But that these formulæ do not correspond to bibromo-succinic and isobibromo-succinic acids is plain from the following considerations. These acids are formed by the direct addition of bromine to maleic and fumaric acids. The bromine must, therefore, be combined with the two carbon equivalents, which in maleic and fumaric acids are combined together, so that the latter of the two formulæ given above must be that of both brominated acids.

8. As the constitutional formula for succinic acid shows no difference as to "chemical position" among the four atoms of hydrogen in the radical, there can be only one formula for the substance produced, by replacing one of these atoms by the water residue; but we have two varieties of malic acid, active and inactive; these must therefore be absolutely isomeric.

9. The same argument applies to the case of active and inactive aspartic acids; aspartic acid being succinic acid in which one atom of radical hydrogen has been replaced by the ammonia residue NH_2.

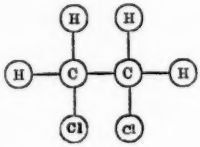
10. As there are two possible formulæ for bibromo-succinic acid, there are also two for tartaric, or dioxy-succinic acid. We have not the same reason for excluding either of these in this case as in that of the bibrominated acids;* but as we have three undoubtedly different varieties of tartaric acid (excluding racemic acid), two of these at least must have one of these formulæ in common.

So far we have been concerned with pairs of substances which seem to be really absolutely isomeric. The remaining substances in our list are more probably metameric.

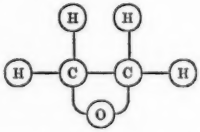
11. If we consider the various reactions of the ethylene compounds, particularly the formation of glycollic acid from glycol, we are forced to the conclusion that the two unsaturated equivalents of the radical ethylene belong to two different carbon atoms. This conclusion may also be arrived at in another less satisfactory way.

* It would be interesting to compare the properties of the tartaric acid formed from isobibromo-succinic acid with that from bibromo-succinic, and with the varieties obtained from the grape.

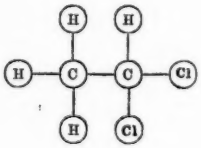
As chloride of ethylene is formed by the direct union of chlorine and ethylene, the chlorine must be combined with those carbon equivalents which in ethylene gas are combined with one another; but equivalents of the same atom cannot be combined with one another, therefore in chloride of ethylene the two atoms of chlorine must be combined with different carbon-atoms. The constitutional formula of chloride of ethylene is therefore—



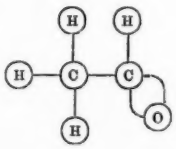
and that of oxide of ethylene



Again, the reactions of aldehyde, the oxide of ethylidene, lead to the view of its constitution first proposed by Kolbe, and now almost universally adopted, $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$ CO, in which both oxygen equivalents are combined with the *same* carbon atom. The constitutional formula of chloride of ethylidene is therefore



and that of aldehyde

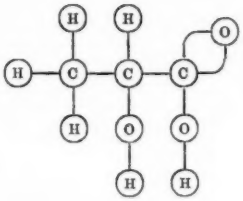


These two series of substances are therefore metameric.

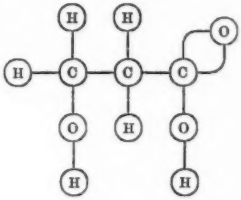
12. The researches of Wislicenus (Ann. Ch. Pharm. cxxviii. 1), and Lipmann (Ann. Ch. Pharm. cxxix. 81), prove that lactic acid and paralactic acid stand to one another in a relation similar

to that of chloride of ethylidene and chloride of ethylene; that, in fact, the former is a compound of ethylidene, with the water-residue and the group $\left(\begin{matrix} H'O \\ \end{matrix} \right\} C''O \Big)'$ and the latter of ethylene with the same radicals. They have therefore the following constitutional formula and are metameric :—

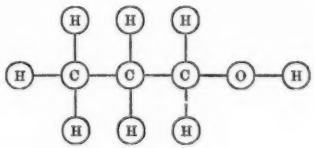
Lactic.



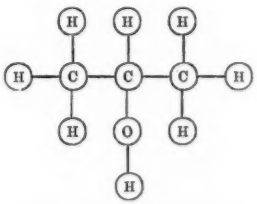
Paralactic.



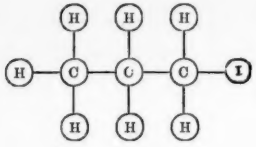
13. With regard to the two series of alcohols—the alcohols proper and the hydrates of the olefines—we know, at least, that Friedel's alcohol is not absolutely isomeric with propylic alcohol, but, as suggested by Kolbe, only metameric. If we consider the relation of these alcohols to their aldehydes—propionic adehyde, and acetone, the aldehyde of Friedel's alcohol—we easily see that the formula of propylic alcohol is



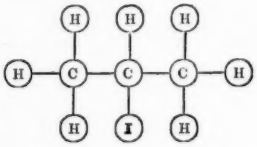
while that of Friedel's alcohol is



As Friedel's alcohol is identical with that obtained by Berthelot from propylene, it is highly probable that the same difference exists in the case of all the other members of the two series. In the same way the iodide of propyl is—



and the hydriodate of propylene



14. As to the aromatic alcohols and the isomeric acids, we know too little of their constitution to speak definitely with regard to their relation. They may, as suggested by Erlenmeyer (Zeitschrift, vii. 12), be absolutely isomeric, or, on the other hand, they may be related to one another as the two series of alcohols last mentioned are.

Having enumerated the bodies which may without hesitation be called absolutely isomeric, I shall now consider the bearing which the existence of such substances has upon the theory of atomicity.

If we examine the fundamental definitions of that theory, we shall see that there is a point of importance left undecided. We define a multequivalent atom as an atom having two or more equivalents, by means of which it may unite with the equivalents of other atoms, but it is not decided whether these equivalents are similar to one another or not. On the former supposition, there can be only one substance corresponding to each constitutional formula, and absolutely isomeric compounds are impossible. It must, therefore, be rejected, as such compounds exist. We must then assume that some of the equivalents of at least some multequivalent atoms are different from other equivalents of the same atoms.

This assumption may take one of two forms—1. We may suppose that the difference is an essential and unchangeable one; that, for instance, the two equivalents of a diatomic atom differ from one another as chlorine does from bromine; and that the one can no more be changed into the other, than an atom of chlorine can be changed into an atom of bromine; or, 2. We may suppose that such a change is possible.

Our knowledge of facts is not as yet sufficiently extensive to enable us to decide definitely between these two hypotheses, but it may be of some use to examine their consequences.

The second is, as yet, obviously too vague and indefinite to admit of this, I shall therefore confine my remarks to the first. The principal advocate of this hypothesis is Professor Erlenmeyer of Heidelberg. Professor Butlerow, of Kasan, has also published some speculations in the same direction; and in his paper on Organic Acids in the supplementary volumes of Liebig's "Annalen," Professor Kekulé, of Ghent, treats shortly on the same subject. The only attempts, however, to apply this hypothesis in a definite way to the explanation of particular cases of absolute isomerism are, as far as I am aware, 1. That of Professor Kolbe, who applies a form of this hypothesis to the case of the isomerism of oxide of ethylene and aldehyde. I have already given my reasons for believing that these substances are metameric, and shall therefore not discuss the point further here. 2. That of Butlerow (Zeitschrift, v. 301), who endeavours by means of it to explain the isomerism of hydride of ethyl and methyl gas; and 3. That of Kekulé (Ann. Ch. Pharm., Suppl. ii. 111), in his explanation of the isomerism of maleic and fumaric acids, and of citraconic, itaconic, and mesaconic acids.*

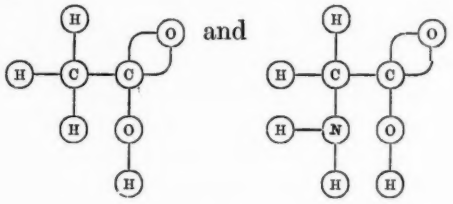
I shall examine the 2nd and 3rd of these examples in detail, and think I shall be able to show a certain degree of inconsequence in both. Professor Butlerow argues, that in methyl gas the two atoms of carbon are combined by two affinities of the same kind (secondary affinities), each being the affinity which in iodide of methyl is combined with iodine. In hydride of ethyl, the two carbon atoms are combined in the same way as in the other members of the ethylic series, therefore, probably in the same way as in the members of the acetic series, one of which is acetonitrile, which is cyanide of methyl; the one is, therefore, the free affinity of methyl (secondary), the other the free affinity of cyanogen. These must be different, because hydride of ethyl is not identical with methyl gas. Butlerow indicates this, by calling the free affinity of cyanogen primary. We have thus in methyl gas two secondary affinities united together, and in hydride of ethyl a primary united to a secondary.

* I do not here notice the remarks of Professor Kolbe (Zeitschrift, vi. 13) on the same subject, as his object is rather to prove the metamerism than to explain the isomerism of these bodies.

In this reasoning we have three assumptions—1. That the nature of the carbon affinities is unchangeable; 2. That the carbon atoms continue united together by the same affinities through a series of chemical reactions, such as the transition from aceto-nitrile to hydride of ethyl; and, 3. That hydride of ethyl is not identical with methyl gas.

By carrying this argument a little further, and making use of no additional assumption, we arrive at an absurdity;—thus, the carbon-radical of the acetic series is the same as that of oxyacetic (glycollic) acid, that again is the same as that of oxalic acid, therefore as that of oxalic nitrile or cyanogen gas; but in cyanogen gas we have the two carbon atoms united by two *primary* affinities; but we have before proved, that in the acetic series they are united by a primary affinity of the one, and a secondary affinity of the other. It is obvious, then, that at least one of our assumptions is false. And when we closely examine the two general assumptions (1. and 2.), we shall see reason to believe, that neither of them is rigidly true.

It is well known that the replacement of one equivalent in a compound by another, while it leaves the "chemical structure," or "chemical position" of the other atoms unchanged, exerts an influence on the *intensity* of the chemical attraction, not only of the equivalents directly concerned in the replacement, but of all the equivalents in the molecule.* To see this we have only to compare the nature of the force uniting H to O in acetic acid, and in glycocoll,



We here see the hydrogen and the ammonia residue NH_2 exerting a "disturbing" influence on the relation of oxygen to hydrogen through two carbon-atoms. Many other examples will at once

* Butlerow notices this disturbing influence (Zeitschrift, vi. 516) as opposing an obstacle, which he seems to regard as for the present insuperable, in the way of determining whether a difference exists or not among the equivalents of a mult-equivalent atom.

occur to every chemist. The nature of the equivalents, that is, of the force they exert, is thus seen to be variable; but the facts of absolute isomerism force us to admit, that this variation in the character and intensity of the chemical force exerted by the different equivalents of one atom depends upon something else, as well as upon the nature of the other equivalents with which that atom is united.

We find, then, that although the nature of one equivalent of an atom does change, as the other equivalents are united with different substances, there must be some original difference between them, which renders absolute isomerism possible. In what this original difference consists, whether it is essential or merely accidental (using the word in its strictly logical sense), we cannot as yet say.

We may thus divide the force uniting any two equivalents, into two components, one depending on the structure of the molecule, and the position of the equivalents in question in it, and the other independent of these. For convenience we may call the first the molecular, and the second the atomic component.*

From all that we know of the disturbing effect of an equivalent on the relations of the other equivalents in the molecule, we may safely assume that the *molecular* component of the force uniting the two carbon-atoms to form the hexatomic carbon radical $(C_2)^{vi}$, is not the same in any two compounds. And if there be more than one body having the formula C_2H_6, we are forced to the conclusion, that in these cases at least, the atomic component is different also.

The question in reference to the second assumption mentioned above may now be stated thus—Does the atomic component of the force uniting the two carbon atoms remain the same through such a series of transformations as that connecting acetonitrile and hydride of ethyl? There is every reason to suppose that it does, if it is always the same for the same pair of equivalents; for there is nothing in any of these transformations which would lead us to suppose that one carbon equivalent has changed places with another. We are then brought to the dilemma, either methyl

* The term component is, of course, not used here in its strictly dynamical sense, what is meant is, that the total force uniting a pair of equivalents, is a function of two quantities, the one depending on the structure of the molecule, and the position in it of the two equivalents, and the other on the chemical nature of the two equivalents.

gas and hydride of ethyl are identical, or a change takes place in the atomic component of the force uniting the two carbon-atoms in some of the transformations connecting cyanogen gas and hydride of ethyl.

In connection with this, it may be proper to examine shortly the relations between the view of the chemical nature of carbon provisionally adopted by Butlerow, in the paper referred to above, and that of Kolbe, as explained in his "Lehrbuch der Organischen Chemie," and in several valuable papers in Liebig's "Annalen," and in Erlenmeyer's "Zeitschrift."

Professor Kolbe considers carbon (carbonyl = (C_2), $C = 6$) as a tetratomic element (as indeed it is now admitted by every one to be), and holds that in a large number of organic compounds, the four equivalents united to the carbonyl atom may be divided into two groups—the intra-radical and the extra-radical—so far his view resembles that of Butlerow; but it differs from it in the following respects:—Butlerow assumes that it is an essential property of the carbon atom to combine in this way, that carbon *always* combines with two equivalents in one way, and with two others in another way. Kolbe only admits this in the case of bodies derived from dibasic carbonic acid. In methylic compounds, for instance, he regards the three atoms of hydrogen as precisely similar. When we examine the theories more closely, we see another reason to doubt their identity. If we try to compare them, we find it difficult to decide whether Butlerow's primary affinities correspond to the intra-radical or extra-radical affinities* of Kolbe; for instance, in formic acid,—$C\begin{cases}H\\O''\\OH\end{cases}$ or $C_2\begin{cases}O_2\\H\\O\cdot H\,O\end{cases}$, the H and the OH (or $O\cdot H\,O$) are united to the extra-radical affinities; but by carrying out Butlerow's reasoning, we are led to the conclusion, that the H is united to a primary, and the OH to a secondary affinity, unless we suppose that the free affinity of methyl is different from that of formyl.

It is not impossible that such a difference may exist, but till this point is settled, and till we know whether the two free affinities of $(CO)''$ are similar or not, it is impossible satisfactorily to compare the two theories.

* I use the terms intra- and extra- radical affinities, as abbreviations for the carbon affinities with which the intra- and extra- radical oxygen atoms are combined.

The other attempt mentioned above to explain cases of absolute isomerism, in harmony with the theory of atomicity, is that of Professor Kekulé.* After shortly recounting the principal facts, more minutely described in his admirable researches on organic acids, he says—"All these facts find, in my opinion, to a certain extent, their explanation in the following considerations:—According to the views on the atomicity of the elements which I communicated some time since, succinic acid and its homologue pyrotartaric acid may be regarded as closed molecules, that is, all the affinities of the atoms composing the molecule are saturated by other atoms. Both acids contain two atoms of hydrogen replaceable by radicals, because two atoms of hydrogen are united to the carbon group by means of oxygen. These two replaceable (typical) atoms of hydrogen may be easily exchanged for metals, because, besides the two atoms of typical oxygen (*i.e.*, oxygen united by only one affinity to carbon), there are other two atoms of oxygen united to carbon by both affinities, which, therefore, in the language of the typical theory, belong to the radical. If these two atoms of hydrogen are represented apart from the rest, as is done by means of the typical formulæ—

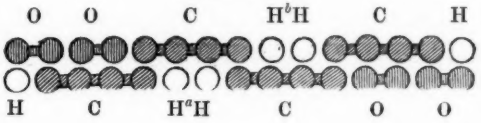
$$\left.\begin{matrix} C_4H_4O_2 \\ H_2 \end{matrix}\right\} O_2 \qquad\qquad \left.\begin{matrix} C_5H_6O_2 \\ H_2 \end{matrix}\right\} O_2$$

or still more clearly by the graphic representations which I have made use of more than once in another place,† it will be readily seen that in succinic acid there are four, and in pyrotartaric acid six, other atoms of hydrogen present. This hydrogen is con-

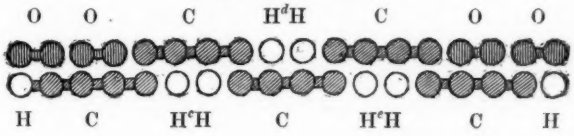
* *Loc. cit.*

† In order to elucidate this passage as much as possible, I append the graphic representations referred to:—

Succinic Acid.



Pyrotartaric Acid.



sidered, according to the typical theory, to belong to the radical, according to the theory of atomicity, to be directly united to the carbon, and in such a way that there are always two atoms of hydrogen united to the same carbon atom. If we now suppose that in the one or the other of these two normal acids two such hydrogen atoms are wanting, we have, on the one hand, the composition of fumaric and maleic acids, on the other, the formula of citraconic itaconic, and mesaconic acids. Now, as there are in succinic acid *two* pairs of hydrogen united in this way to carbon, we easily see the possibility of the existence of two dehydrogenated acids, as the one or the other of these pairs of hydrogen atoms is absent.

"Similarly, in the case of pyrotartaric acid, the existence of three isomeric dehydrogenated acids is intelligible, in each of which another of the three pairs of hydrogen atoms directly united to carbon is absent. At that place in the molecule where the two hydrogen atoms are wanting, there are two carbon affinities unsaturated, there is at that place, so to speak, a blank."*

There is some difficulty in understanding this last statement. For what can be meant by two affinities of the same carbon atom uniting together? unless the definition of either "atoms" or "combination" be completely changed. Or if we take the natural meaning of the sentence last quoted, and suppose two carbon-atoms pushed together, so that two affinities of each previously united to hydrogen come to be united together, the two wanting hydrogen atoms do not come from the same, but from two different carbon-atoms.†

But leaving this preliminary difficulty out of consideration, and also granting the existence in such a molecule of diatomic carbon, a glance at the diagrams is sufficient to show that this view does not give us two but only one formula for fumaric and maleic acids, unless a difference be admitted among the affinities of carbon. The pairs of hydrogen-atoms, which I have marked *a* and *b*, have perfectly similar positions, the one being related to one end of the diagram, exactly as the other is to the other end. In the same way the graphic representation of pyrotartaric acid suggests only two formulæ for citraconic, itaconic, and mesaconic

* "It may of course equally well be assumed, that the carbon-atoms are, as it were, pushed together (zusammengeschoben), so that two carbon atoms are united by two affinities of each. This is only another form of the same idea."

† See Erlenmeyer, Zeitschrift, vi. 21.

acids, there being no apparent difference between the position of the pairs *c* and *e*.* This explanation is insufficient, not to say unintelligible, unless we suppose a functional difference between the two carbon-atoms, with which the pairs of atoms of hydrogen are united; and if we make this assumption, it follows as a necessary consequence that there is a difference between the two groups of HO. It is no doubt possible that such a difference may exist; but it seems very unlikely that such a property of a substance so well known as succinic acid should not have been observed.

We thus see, that the attempts to apply to the explanation of particular cases the principle of a difference between the equivalents of multequivalent atoms have failed, not, however, as far as can at present be seen, from any absurdity in the principle itself, but rather from a want of well-observed facts to guide us in its application. These we may expect before long, from the labours of Buttlerow, Schorlemmer, and others, and we shall then be in a position to form a definite opinion as to the form which this hypothesis should assume.

XXXVIII.—*On the Action of Light upon Sulphide of Lead, and its bearing upon the Preservation of Paintings in Picture Galleries.*

By Dr. David S. Price, F.C.S.

[Read before the Chemical Section of the British Association at Birmingham.]

My attention was directed to the action of light upon sulphide of lead from observing that in the glass cases in the Technological Museum under my charge at the Crystal Palace, which are painted white with white lead, substances which emitted sulphurous vapours did not cause a darkening of the surface of the case, except where it was protected from the direct influence of light.

In the case devoted to sulphur, for instance, the spaces obscured by the descriptive cards alone were blackened, the white colour of the rest of the case being unimpaired. In the cases containing vulcanized india rubber, wools, woollen fabrics, hair, and other animal products containing sulphur, the same appearances were presented.

* See Buttlerow, Zeitschrift, vi. 524.

In the first named of these cases I had placed the dried leaves of the gutta-percha plant, attached to a piece of cartridge paper—a translucent substance. Upon removing the paper I found a tolerably faithful photograph of the leaves upon the surface of the case.

In order to verify these observations, and to gain a knowledge of the cause and rapidity of the action, and at the same time to ascertain the effect of the coloured rays upon sulphide of lead, the following experiments were made:—

A board painted white with white lead and oil was exposed in a chamber for several hours to the action of sulphide of hydrogen gas, until the painted surface had acquired a nearly uniform chocolate, or deep-brown hue. Plates of glass of different colours were then placed upon the painted surface, one portion being at the same time covered by an opaque medium, and another left open and unveiled to the light. The board was then placed in a situation facing the east.

The glasses which I employed were of the following colours and properties: 1, red; 2, blue; 3, yellow; 4, violet; 5, a glass that diminished the intensity of all the rays; and 6, a glass which slightly reduces the yellow ray. My friend Mr. Robert Hunt, F.R.S., was kind enough to lend me the series of coloured glasses which he employed in his investigations for the British Association, and the optical properties of which he had determined, but with the above exceptions I have not thought it requisite to record the results obtained, desiring rather to view the subject from a practical point. The results shown are from an exposure of eight days, on one of which only was the atmosphere clouded. It will be observed that the surface exposed to the action of the light is now perfectly white, whilst that under the influence of the red ray remained as dark as where the sulphide had been protected from light. The blue ray has effected an almost complete conversion of the sulphide; the yellow ray a partial, and the violet considerably less action than the yellow. The light passing through glass 5 has produced somewhat less effect than has resulted from the blue rays, whilst with glass 6 the action has been nearly as rapid as where the surface has been left quite exposed to the light. The action of drying oils is very rapid upon sulphide of lead, an exposure to light for a few days only being sufficient to change a surface of it coated with a thin layer of linseed oil into a white one. When boiled linseed oil is

used, still less time is required to effect the change. That the action is an oxidising one there can, therefore, be little doubt, and I regret that I have not been able to get the further proofs on this point ready for this occasion, but knowing that there are many in Birmingham who might be interested in the subject, I have thought it better not to defer the communication of these results on that account. It is, however, not only when mixed with oil that the conversion of the sulphide is accomplished, for where water colour was used, the action was still marked, although slow, as will be seen by the illustration exhibited, in which the dark spaces were protected from the light by cards and other opaque substances.

These observations serve to explain part of the evidence given before the "Royal Commission appointed in 1857 to report upon the site best adapted for the National Gallery," in reference to the facts stated by directors of galleries, artists, and picture-dealers, as to the injury which pictures suffer by being kept in ill-ventilated and badly lighted places, and of the beneficial effects resulting, in many instances, from the exposure to direct sunlight of injured pictures.

From this report I will quote the following:

Mr. Knight, the Secretary of the Royal Academy, stated that he preferred pictures to be exposed to the light if he wanted to preserve the lights of a picture.

Mr. Farrer mentioned a case where, by exposing a picture that had been kept in the dark, the blue became brighter.

Sir Charles Eastlake, P.R.A., instanced the case of some of the pictures from the late Mr. Turner's gallery, those of "the Deluge" and "Queen Mab," in particular, where the whites were turned into blacks, and stated that white lead, if not tolerably well secured from the effects of the atmosphere, would undergo a rapid change in London, and that it was a very general opinion that pictures look better and last longer in the country than in London.

Mr. Bentley, who restored these pictures by a secret and chemical process, said that the highest light was perfectly black, and that, in fact, "high light" was "high dark."

I have here an illustration to show that the changes effected by the secret and chemical process may be brought about by simple exposure of the picture to the light. The picture was placed in an atmosphere of sulphide of hydrogen gas until it had acquired

a dark brown colour. Strips of paper were then fastened across parts of the surface, and it was placed in a window facing the light. Those portions not obscured, it will be observed, have resumed their original appearance, whilst those covered by the paper remain as black as when the paper was first placed over them.

Mr. Cooke, R.A., stated that light is one of the greatest agents in the preservation of pictures; that it helps to develope them in every way, particularly with regard to the varnish, and he gave an instance of a picture of his own which he had lent for exhibition to a gallery where it had been exposed to a very strong light; that five months afterwards, when it was returned to him, he was surprised at its extremely bright appearance.

In reference to the action of light on varnish mentioned by Mr. Cooke, I may observe that I have found that when light is excluded from a painted white surface, the surface assumes a dingy yellow colour, but that the original colour is restored by admitting the light to it. This fact is, I find from the report, acknowledged by many artists.

I have said that the glass cases containing woollen fabrics were blackened, and it may be well to draw attention again to the fact, with a view of showing that no small source of sulphur vapour in the atmosphere of a gallery frequented as the galleries in London are, may arise from the clothes of the visitors.

That the experiments which I have described, taken in conjunction with the testimony just read, have an important bearing upon the preservation of paintings, will, I think, be evident, as they demonstrate the protecting influence of light upon white lead and those colours with which it is mixed, where the atmosphere is or may become contaminated with sulphurous gases, and conversely the deterioration that paintings must suffer where under the same circumstances the light admitted is feeble—facts deserving of attention in the construction of galleries in the metropolis and large manufacturing towns, and by those who have the care of paintings in churches and public buildings, or who possess collections of their own, and adopt the practice of covering their pictures.

It is curious to observe in many parts of London the discolouration of houses painted with white lead. I have frequently seen the lower portions completely coated with a metallic-like surface of the sulphide, and I have little doubt that the formation

of this compound will be found to be more frequent in winter than in summer, and more prevalent on the shady than on the sunny side of a street.

XL.—*Notes on the Compounds of Copper and Phosphorus.*

By F. A. Abel, F.R.S.

About six years ago, I commenced a series of experiments upon the combinations of phosphorus with copper, having been led to undertake them by a suggestion made to Colonel F. Eardley Wilmot, then Superintendent of the Royal Gun Factories at Woolwich, by Sir Henry James, R.E., that phosphorised copper might be found to possess advantages as a material for ordnance, over the copper and tin alloy popularly known as gun metal. These experiments were carried on occasionally during about three years, and some of the results, of a scientific character, furnished by them induced me to attempt a general investigation of the phosphides, the chemical history of which, though it has received many important contributions from chemists of eminence, is still far from complete. My experiments in this direction have, however, met with such frequent and protracted interruptions that I was compelled, some considerable time ago, to abandon this interesting subject for research, more particularly as several of the results arrived at by me, now some years ago, have been since obtained and published by other chemists. I now venture to offer, in the form of Laboratory Memoranda, a few experimental observations upon the properties of some of the phosphides of copper, and of that metal combined with only small proportions of phosphorus.

The correctness of the statements made by H. Rose with regard to the formation of the two phosphides of copper, having the respective compositions Cu_6P and Cu_3P, have been confirmed on more than one occasion. The lower phosphorus-compound is described by that chemist as being produced by the action of phosphoretted hydrogen upon the disulphide or dichloride of copper, and also by strongly heating the triphosphide of copper in hydrogen. The triphosphide is formed by passing phosphoretted hydrogen over the protochloride of copper, and also by acting with the gas upon a solution of sulphate of copper.

The results obtained by me in experiments on a method given by Rose for the production of the diphosphide of copper Cu_2P,* do not agree with those described by him. Upon exposing the diphosphate of copper to the action of a current of hydrogen at the strongest red heat that the glass tube will sustain, Rose states that the copper-salt first turns yellow, from formation of dioxide of copper, and is subsequently converted, with formation of water, into the diphosphide, which becomes crystalline on cooling. I have several times repeated this experiment, and on no occasion have I been successful in obtaining products which contained a higher proportion of phosphorus than that existing in the hexaphosphide (Cu_6P); indeed, the proportion of phosphorus contained in the product, after purification, was generally much below that contained even in this phosphide, while a considerable proportion of phosphoric acid was always liberated. Thus, in one experiment in which the diphosphate was exposed for some time to a red heat, in a current of hydrogen, the product, which was deliquescent, contained, after purification, eight per cent. of phosphorus. By submitting small quantities of the diphosphate to the action of dry hydrogen in a hard glass tube, at the highest temperature which the latter was capable of sustaining, copper-coloured products were obtained, which, upon treatment with water, broke up into brilliant spangles. These were examined after separation of the free phosphoric acid, and were found to contain only three per cent. of phosphorus.

The impossibility of producing the diphosphide in the manner described by Rose is demonstrated, moreover, by the effect of heat upon that phosphide itself. When heated for some time to full redness out of contact with air, it is reduced to the hexaphosphide (Cu_6P). This reduction was effected in my experiments by heating 1543·235 grammes of the diphosphide in a closed porcelain crucible, which was enclosed in a Hessian crucible compactly filled with powdered charcoal. After exposure in a furnace to a bright red heat for three or four hours, the crucible was allowed to cool. The interior surface of the porcelain was uniformly blackened, as though from reduction of silicon in the glaze by the phosphorus. The grey button of fused phosphide at the bottom of the crucible weighed 1041·66 grms.; there were, in addition, a few very small beads adhering to the sides of the crucible.

* Pogg. Ann. 24, 231. Gmelin, 5, 417.

The product was found to contain 14·2 per cent. of phosphorus; the theoretical percentage in the hexaphosphide is 14·01.

The diphosphide is similarly reduced to hexaphosphide when heated in a current of hydrogen. The examination of several products obtained by exposing the diphosphide to a red heat in a current of that gas, furnished numbers closely agreeing with those required by theory for the formula of the hexaphosphide. The gas escaping from the apparatus during these experiments was endowed with interesting properties. It contained a small proportion of phosphoretted hydrogen, but it was also mixed with phosphorus vapour, in proportion varying with the temperature and period of the operation. Occasionally it was spontaneously inflammable, furnishing the rings of vapour which are produced when bubbles of phosphoretted hydrogen are burned. At other times, though it did not inflame upon passing into the air, if it were allowed to impinge upon paper or the hand, or if placed under some pressure before being allowed to escape through mercury or water, the gas would ignite. Or, if allowed to escape in bubbles, it would, without inflaming, gradually furnish wreaths like those produced by phosphoretted hydrogen, which were, however, beautifully phosphorescent in the dark. Similarly, if a jar of the gas were collected over water and then exposed to air, the contents of the jar became phosphorescent as the air gradually entered. Upon allowing the gas to stand for some hours over water, minute particles of phosphorus were deposited, and it lost its phosphorescent power. This gas furnished brown or black precipitates with solutions of lead, copper, bismuth, silver, and mercury. The quantities of these precipitates obtained were insufficient for analytical purposes.*

The foregoing experiments demonstrate that the hexaphosphide (containing 14 per cent. of phosphorus) is the highest copper-compound which is susceptible of production at a red heat, or capable of resisting the expulsion of phosphorus by exposure to that temperature.

The following are some experiments made on the direct union of copper with phosphorus.

Upon heating clean copper turnings in a hard glass tube to low

* By passing hydrogen over boiling phosphorus, or over amorphous phosphorus heated to the temperature at which its conversion into ordinary phosphorus commenced, the gas was similarly impregnated with phosphorus vapour, being rendered spontaneously inflammable and blackening lead- and silver-solutions.

redness, and then passing phosphorus-vapour over them, they became incandescent, and furnished a fused steel-grey mass, presenting here and there a brilliant crystalline appearance upon the surface, and so brittle as to be easily pulverised. This product, which was dissolved without difficulty in concentrated nitric acid, contained 12·2 per cent. of phosphorus. When powdered and heated to bright redness in a narrow glass tube, closed at one end, it fused, and sustained no loss of phosphorus. In another experiment, some portions of the product contained 13·8 per cent. of phosphorus.

Attempts made to add to fused copper in a crucible the maximum proportion of phosphorus with which it would combine, did not furnish very uniform results, owing to difficulties of manipulation, but indicated that about 12 per cent. was the highest proportion with which the fused metal can be made to unite.

In one operation, carried on with about six pounds of very pure Australian copper, in a clay crucible, the metal, when thoroughly liquid, was allowed to cool down very slowly in the furnace, phosphorus being thrust beneath the surface, piece after piece, and stirred into the metal until the product began to solidify. The cold mass, upon being broken under a steam-hammer, was found to consist of three products. The upper layer presented a bright crystalline fracture, and consisted of a brittle, very hard alloy, similar in appearance to white iron, the phosphorus in which amounted to 12·05 per cent. The central and principal portion of the product presented a greyish, very close-grained fracture, was also very hard and brittle, and contained 6·08 per cent. of phosphorus. The third layer, which was at the bottom of the crucible, was only very small; it was broken with difficulty, being extremely tough; it retained the original characteristics of the metal, and contained only 0 47 per cent. of phosphorus.

In another operation, conducted in a similar manner, three products were again obtained, of which that at the top of the crucible contained 7·54 per cent. of phosphorus, while the central layer contained 4·07 per cent., and the small layer of metal at the bottom of the crucible 0·5 per cent. Several other experiments furnished similar results.

Several methods were tried for producing a phosphorised copper, in moderately large quantities, of uniform composition. Copper turnings were heated in a skittle-pot to dull redness, and pieces of

phosphorus were then thrown in. The latter combined with the metal without much waste of phosphorus, and a very liquid product was obtained, which, after a definite quantity of phosphorus had been added, was poured off from a small portion of the copper which had not been fused, into iron moulds. The ingots of metal obtained were hard, very close-grained and resembled bell-metal in their fracture, which speedily tarnished. The proportion of phosphorus they contained in different operations varied between 3·9 and 4·7 per cent. In one operation, conducted at a lower temperature than usual, a product containing 5·74 per cent. of phosphorus was obtained.

In other operations, scrap-copper, in pieces of moderate size, amounting to about 25lbs., was heated to full redness in a crucible, and the phosphorus was then gradually added. In order to avoid loss of phosphorus, and to render the handling of that substance safe in the hands of the workmen, it was cut into pieces about one inch in length, and immersed for a short time in a solution of sulphate of copper. The phosphorus thus became enveloped in a coating of copper, which protected it from contact with air, and allowed of its being thrust below the surface of the melted metal without loss. The product was always cast while a portion of the copper still remained solid. By this method, products containing from 2·75 to 4 per cent. of phosphorus were obtained. These were afterwards re-melted with the requisite proportion of copper to furnish products for experiment, containing from 1 to 3 per cent. of phosphorus.

The presence of even one-half per cent. of phosphorus in copper increases its fusibility considerably, and renders it more limpid, so that it flows into moulds readily. If cast in iron moulds (or chills), very considerable contraction takes place, during solidification (according to the proportion of phosphorus present), and perfectly sound castings of very compact structure are obtained. But if the moulds are of sand or loam, the casting is always porous and defective.

The tenacity of copper is considerably increased by the presence of even a small proportion of phosphorus (0·5 per cent.), provided the metal be cast in a chill.

The following is a statement of the weights sustained at the moment of fracture, by specimens of cast metal containing different proportions of phosphorus, in comparison with the average "breaking weights" of gun-metal, and of specially selected ingot-copper

of high quality (Australian and Swedish). The specific gravities of the specimens and their comparative extension at the moment of fracture are also given.

Description of Specimens.	Breaking weight per square inch.	Extension upon the inch at moment of fracture.	Specific gravity.
Ingot copper } Various }	24,991 lbs. to 26,424 „		8·793 to 8·891
Gun-metal— (average of many experiments)	32,000 „	0·25 inch	8·45
Phosphorised copper— containing 0·5 per cent. phosphorus	38,389 „	0·55 „	8·876
containing 0·75 per cent. phosphorus	44,373 „	0·345 „	8·815
ditto ditto	45,568 „		
containing 1·45 per cent. phosphorus	45,369 „	0·24 „	8·614
ditto ditto	45,737 „	0·23 „	8·580
containing 1·75 per cent. phosphorus	47,663 „	0·26 „	8·615
containing 2·5 per cent. phosphorus	47,908 „	0·10 „	8·422
containing 1 per cent. phosphorus imperfect bar (cast in iron mould)	36,893 „		
portion of the same metal cast in sand	19,942 „		
ditto ditto	16,951 „		
ditto ditto	13,959 „		

The last four numbers are quoted to illustrate the great influence exerted upon the strength of the metal by the manner in which the casting has been produced. It is evident, therefore, that in attempting to apply phosphorised copper to the military uses of the gun-metal alloy, it must not be cast in sand or loam, like the latter.

The mechanical experiments instituted with the phosphorised copper indicated that the best results, as regards tenacity, might be expected from metal containing from 1 to 1·5 per cent. of phosphorus. When the proportion of the latter exceeded 2 per cent. the hardness of the metal increased considerably, while its tenacity was not greatly added to.*

The great compactness of structure of the phosphorised copper, containing only 0·5 per cent. of phosphorus, and the comparative malleability of this particular variety, led to some experiments with a view of applying it as a material for the breech-rings or washers

* The substitution of wrought-iron rifled guns for the Service "brass" field guns, brought to a close the experiments on the application of phosphorised copper as a material for ordnance.

used in the Armstrong breech-loading cannon. It was sought, before hammering this metal into the form of rings, to increase its toughness by rolling. For this purpose several cylindrical bars of phosphorised metal, four inches in thickness, and about four feet long, were prepared. The metal was produced from Lake Superior ingot copper, which was submitted, in quantities of about 56 lbs., to the treatment with phosphorus described. The metal was afterwards re-melted and cast into vertical iron moulds; it shrunk very considerably, and was "pumped" during the cooling to promote the formation of perfect bars. The phosphorus in these bars amounted to 0·58 and 0·35 per cent. The rolling experiments were made with them by me at the Government Mills at Chatham. The very red-short character of phosphorised copper, pointed out by Percy in the article on copper and phosphorus, in his work on Metallurgy, was strikingly illustrated by the first rolling experiment, instituted with a bar containing 0·58 per cent. of copper. The metal was heated in an annealing furnace up to redness barely visible in the dark, it was then allowed to cool down in the air for a quarter of an hour, and passed through rough rolls with only a slight grip. As the bar was carried through it was completely broken up, the fractures on either side of the bar being coincident with the ridges of the rolls.

The other bars were rolled carefully, quite cold, between smooth rolls, and were annealed after having been passed five or six times through the rolls. In this way the four-inch bars were rolled out to bolts of $3\frac{5}{8}$ inches diameter, but not one of them was perfectly sound throughout, the rolling having been stopped, indeed, when slight cracks were perceptible in one or two parts of the bolts.

Sound portions of these bolts were afterwards converted into breech-rings for Armstrong guns in the same manner as these are produced from copper bolt, namely, by hammering out, cold, a piece of the perforated bolt. The metal was reported to work exceedingly well under the small tilt hammer used; but, when tried in the guns, it was found to be rapidly worn away by the combined effects of the heat and the mechanical action of the gas.

Some experiments were made on the production of small castings, for fittings, from phosphorised copper containing about 1 per cent. of phosphorus, but the impossibility of producing sound castings in sand, and the great shrinkage of the metal when cast in iron moulds, precluded its application in this direction.

It is pointed out by Percy, in the account of his experiments on

the combinations of copper and phosphorus (originally published in the "Chemical Gazette"), that the employment of an iron rod for stirring the melted metal containing phosphorus should be avoided, as iron is readily taken up by the latter. In one or two of my earlier experiments an iron rod was used for the purpose named, and the products, on subsequent examination for iron, were found to contain proportions of that metal ranging from 0·07 to 0·32 per cent. (the percentages of phosphorus in the metal being 0·75 and 1·45 per cent.) The tenacity of these specimens was not found inferior to those in the preparation of which a rod of wood or copper had been used.

It was considered of interest to ascertain whether it be possible to produce alloys containing copper in combination with phosphorus and a considerable proportion of iron.

In one experiment fifty ounces of copper were melted, and two ounces of phosphorus were gradually added in the usual manner. A large proportion of clean wrought-iron shavings was afterwards added, and the contents of the crucible were stirred for some time. The liquid portion was then poured into an iron mould. It was found to divide into two layers; the upper and smaller one was dark grey, hard, and brittle, and contained only a small proportion of copper. The lower layer was found to have the following composition:—

Copper	..	96·67 per cent.
Iron	..	2·45 „
Phosphorus	..	0·88 „

About three-fourths of the phosphorus added to the copper had, therefore, been abstracted by the iron, with which it formed the brittle phosphide referred to above.

In a second experiment 39 ounces of copper were combined with about 1 ounce of phosphorus (a small quantity escaping during the operation) and the product was submitted to treatment with iron, as in the first experiments. Upon breaking the ingot of metal obtained, which again consisted of two layers, the copper-alloy, which constituted the lower layer, was found to contain very small globules of the dark grey iron-product, distributed through it. A specimen of the metal, apparently free from these globules, was selected for analysis, and found to have the following percentage composition:—

Copper.....	97·00
Iron.....	1·66
Phosphorus.....	1·33

Neither of these two products could be submitted to mechanical experiments, on account of the presence of the small globules spoken of. Attempts were made to obtain homogeneous products by remelting the copper-alloy with a considerable additional proportion of copper, but in every instance, a small layer of the iron-product was obtained upon the surface of the cast metal, and minute globules always remained dispersed through the latter.

A third experiment was made with 18 lbs. of phosphorised copper containing four per cent. of phosphorus. A further addition of 6 ounces of phosphorus was made to the metal, but a portion of this phosphorus escaped during the operation. Two pounds of wrought-iron turnings were then added, and the completely melted product, after having been well stirred, was cast in an iron mould. The dark grey upper layer was analysed, as well as the larger product forming the lower layer, a portion of which was selected free from the phosphide of iron. The following numbers represent the percentage composition of each:—

	Lower layer.	Upper layer.
Copper.....	96·00	4·31
Iron.....	3·02	83·30
Phosphorus.....	1·07	11·95

It appears, therefore, that by the addition of iron to phosphorised copper, only a small proportion, from one to three per cent., of the iron alloys itself with the copper, while the phosphorus in the latter is to a very considerable extent abstracted from it, in consequence of its greater affinity for iron. It is possible that the phosphorus passes almost completely into combination with the iron, and that the proportion of phosphorus found in the copper-product exists in the form of a phosphide of iron which is dissolved in, or disseminated in a very fine state of division through, the copper. I had intended to see how far it is possible to separate the phosphorus from phosphorised copper by treatment with iron, but it has not been possible for me to continue these experiments. Percy has described a product obtained by digesting with dilute nitric acid, phosphorised copper (containing

2·41 per cent. of phosphorus) which had been stirred with an iron rod, and contained 2·41 per cent. of that metal. The black powder which this treatment furnished was found to have a composition represented by the formula Fe_5P_2. This formula demands 31 per cent. of phosphorus; it will be seen, therefore, that the grey product obtained in the preceding experiments was a much lower phosphide. The results of its analysis indicate, in fact, that it has the composition Fe_8P. This formula demands 12·17 per cent. of phosphorus, to which number the mean result of analysis, 11·95 p. c., approaches sufficiently near, considering that the phosphide contains a small percentage of copper.

The alloy of copper and tin, known as gun-metal, though no longer employed as a material for ordnance in this country, is used to a very considerable extent in connection with artillery equipment, for the production of fittings to gun-carriages, metal fuzes, sockets for shells and other small objects, some of which, such as the pivots of naval gun-carriages, are required to possess considerable strength. The great variation in uniformity of structure, and consequent strength, of the copper and tin alloy, rendered it desirable to ascertain how far the latter might be improved in these respects, by the addition of a small proportion of phosphorus. The results of several experiments showed that, provided the phosphorised alloy were cast in a chill, the uniformity and strength of the metal were greatly improved, but that its very considerable shrinkage, upon cooling, when thus cast, rendered the production of perfect castings with it, of any but the most simple forms, extremely difficult and uncertain.*

* Since preparing these notes, I have been informed by Mr. Parkes, of Birmingham, that he has been in the habit for many years past of "phosphorising" both the copper and brass used for printing and embossing rollers, boiler-tubes, &c., and that he patented this application of phosphorus, I believe, in 1849. The quantity of phosphorus employed by Mr. Parkes is smaller than the proportions used in my experiments. He adds to the metal, immediately before casting, one quarter per cent. of phosphorus; but the highest percentage of that element found in specimens of the cast metal, with which he furnished me, was 0·18. Mr. Parkes states that the working properties of the metal are greatly improved by this treatment with phosphorus, and that he does not experience the difficulties in rolling his metal, either hot or cold, which I found to exist in working with metal containing about 0·3 p. c. of phosphorus. It appears to me probably that the phosphorus which Mr. Parkes adds to the metal just before casting, acts mainly as a deoxidising agent, and that the improvement in the working qualities of the products are more to be ascribed to this action than to the small proportion of phosphorus retained by the metal.

XLI.—*Chemical Researches on some new and rare Cornish Minerals.*

By A. H. Church, M.A., Professor of Chemistry, Royal Agricultural College, Cirencester.

I. *Hydrated Cerous Phosphate.*

The hydrous phosphate which forms the subject of the present communication, occurs as a thin crust closely investing a quartzose matrix. This crust is made up of very minute crystals, generally occurring in fan-like aggregations of single rows of prisms. The faces of union of these groups are parallel to the larger lateral prismatic planes. Occasionally the structure is almost columnar, or in radiating groups, presenting a drusy surface and a general appearance somewhat resembling that of wavellite. The mode of attachment of the crystals is such that only one of the end-faces of the prisms can be studied fully. It would appear that the crystals belong to the oblique system, and are prismatically developed forms. The end-face, 001, presents the aspect of an unmodified rhomboid; occasionally, however, its diagonally opposite acute angles are replaced. Whether the appearances then presented by the crystal are due to a truncation of the solid acute angle, or to a bevelling of the acute prismatic edge, it is difficult to say, owing to the microscopic size of the crystals, and their parallel mode of aggregation.

The plane of cleavage most easily obtained is parallel to the end-face 001; this cleavage is very perfect. Other cleavages are obtainable; one parallel to the plane previously referred to as replacing the acute solid angles or acute prismatic edges of the crystal, the other parallel to the larger lateral prismatic planes. The crystals are fragile.

Other surfaces besides the faces of union and the flat cleavage planes are occasionally shown in breaking a crystal; these surfaces indicate a distinctly conchoidal fracture.

As seen under the microscope, the crystals are transparent to translucent.

The general lustre of the mineral is vitreous. But the conspicuousness of the end-faces with a brilliant pearly lustre, causes the general aspect of the grouped crystals to be splendent. The crystals are doubly refractive, but owing to their minute size, I have not yet obtained a specimen capable of affording indications

as to the number and direction of the optic axes. For the same reason they have not been examined as to the presence or absence of pleochroism.

The colour of the mineral is a pale smoke-grey, with a faint tinge of flesh-red. The streak and powder are white.

The hardness of the mineral slightly exceeds 3. It distinctly abrades a cleavage-surface of calcite. The density of the mineral has not been determined with exactness. In an experiment with a small fragment, the density was found to be 3·14, but the quantity of the material was quite insufficient for anything more than an approximative result.

The following are the blowpipe reactions of the new species. Heated alone in a tube, the mineral becomes opaque, and gives off water, having a very faint acid reaction. Exposed to the oxidising flame, the mineral becomes reddish in colour, and then presents the difficult solubility of cryptolite. It melts and dissolves completely in borax; in the oxidising flame the colour of the bead is opaline and orange-yellow when hot, and colourless or slightly amethystine when cold.

Half of my specimen of the mineral was carefully removed from the gangue, and then picked over with the aid of the microscope. Portions submitted to qualitative analysis shewed the presence of phosphoric acid, lime and water, also of an earth resembling alumina. But it was soon found that this earth, as precipitated by ammonia, became orange-brown on ignition, and dissolved in hydrochloric acid with evolution of chlorine. The chloride thus formed when heated with oil of vitriol, gave a soluble sulphate, which was at once precipitated by potassic sulphate as an insoluble double salt. In the solution of the chloride, oxalate of ammonia produced a copious pale pink precipitate, curdy at first, but rapidly becoming crystalline. From these indications and the blowpipe reactions, it was evident that the earth resembling alumina was in reality the mixed hydrates of the metals of the cerium group.

The results of the quantitative analyses were perfectly accordant and satisfactory.

A few words as to the processes of separation adopted may not be out of place here.

The mineral was finely pulverised, and the water determined by the loss on ignition. The residue was gently warmed with a few drops of oil of vitriol. When complete decomposition had been

thus effected, the mass was extracted with boiling water; the insoluble residue was insignificant, but was collected and weighed. To the clear, warm solution, containing phosphoric acid, the sulphates of cerium and calcium, and some excess of the sulphuric acid employed, ammonia was added, till a barely perceptible cloudiness was produced, then a few drops of oxalic acid were introduced, and, lastly, excess of oxalate of ammonium. After standing 12 hours, the precipitated oxalates of cerium and calcium were collected on a weighed filter, washed, dried, weighed, ignited, and then weighed again. The ignited mass, which was of a lemon-yellow* tint, was then dissolved in hydrochloric acid, the hydrates of the cerium metals precipitated by ammonia, and then ignited and weighed. The lime was precipitated as oxalate from the filtrate. The phosphoric acid was finally removed as the ammonio-magnesium salt, from the liquid filtered from the original oxalates. In a second analysis the phosphoric acid was first of all separated by the molydic acid method.

The following are the details of the analytical results :—

I.	·534	gramme gave	·241	gramme	$Mg''_2P_2O_7$.
I.	·534	„ „	·051	„	$Ca''CO_3$.
II.	·33	„ „	·05	„	H_2O.
II.	·33	„ „	·178	„	Ce''_3O_4.
III.	·246	„ „	·024	„	$Ca''CO_3$.
III.	·246	„ „	·036	„	H_2O.
III.	·246	„ „	·136	„	Ce''_3O_4.
III.	·246	„ „	·108	„	$Mg''_2P_2O_7$.

The following percentages are deduced from the above numbers :—

	I.	II.	III.
$Ce''O$	—	51·21	52·52
$Ca''O$	5·34	—	5·49
P_2O_5	28·88	—	28·08
H_2O	—	15·15	14·71

* The oxalates of the cerium metals, if a little oxalate of calcium be present, exhibit this lemon-yellow colour on ignition.

† The small quantity of insoluble gangue, mainly silica, left on dissolving the mineral for analysis has been deducted in all cases.

The following are the mean percentages:—

$Ce''O$	51·87
$Ca''O$	5·42
P_2O_5	28·48
H_2O	14·93
	100·70

Assuming the calcium to be an essential and not intruding element in the mineral (and the strict accordance of the two determinations of calcium made in different parts of the specimen confirms the assumption), we may deduce from the analytical results the formula

$$5Ce''O.Ca''O.2P_2O_5 + 8H_2O.$$

This formula demands the following percentages:—

	Theory.		Mean of Experiments.
$5Ce''O$	540	52·73	51·87
$Ca''O$	56	5·47	5·42
$2P_2O_5$	284	27·73	28·48
$8H_2O$	144	14·07	14·93*
	1024	100·00	100·70

Adopting the older atomic weights, the mineralogical formula may be given thus:—

$$(\dot{C}e_{\frac{5}{6}}\dot{C}a_{\frac{1}{6}})_3\dot{\dot{P}} + 4\dot{H}.$$

The oxygen of the base, acid, and water shows the ratio

3 : 5 : 4

resembling in this respect scorodite and possibly hureaulite also, if part of the water in the latter mineral may be regarded as basic.

The present species may be easily distinguished from all the allied minerals by several of the characters already given. The occurrence of a British mineral rich in cerium is, of course, of considerable interest, but the complete novelty of the species as a *hydrated* phosphate of the metal attracts particular attention, the

* The excess of water is perhaps due to hydrofluoric acid, but the proportion of fluorine present is very small, and the formula which its occurrence suggests is not confirmed by the determinations of P_2O_5 or CeO. By analogy the formula which might be proposed is—$3CeO,P_2O_5$ + 4aq. + $\frac{1}{3}CaF_2$.

known phosphates, cryptolite, monazite, &c., being, when quite unaltered and pure, completely anhydrous. Calcium also does not occur in cryptolite, and in monazite never exceeds 1·5 per cent.

The mineral is a Cornish species. It was found by Mr. Talling, of Lostwithiel, some time ago.

It may be as well to add that the mineral under review exhibits no signs whatever of being an altered substance. It occurs in a copper lode on quartz and killas.

II. *Hydrated Calcium-aluminic Phosphate* (*?*).

I lately obtained from Mr. Talling a mass of quartz crystals mixed with iron- and copper-pyrites, partly coated with childrenite, and containing, moreover, in numerous cavities and fissures a light and soft white powder. This powder was found to contain lime, alumina, phosphoric acid, and water, together with a trace of iron. When free from impurities it presents the appearance of a pearly powder of perfect whiteness, rather difficultly soluble in acids. Under the microscope it is seen to consist of minute acicular crystals, transparent to translucent, and fragile. Sometimes these crystals are sparsely scattered in irregular stellate groups upon the quartzose matrix. By very careful selection under the microscope, a sufficient amount of the pure white crystals was obtained for analysis, but the quantity at my disposal was quite inadequate for a determination of density, while the physical condition of the substance precluded me from ascertaining its exact hardness.

The mineral gives no colour (unless childrenite be present) to the borax bead. Heated alone it incandesces and becomes opaque. After ignition it gives a distinct blue colour with nitrate of cobalt.

The following are the results (after deduction of insoluble gangue,* &c.) of the quantitative analysis. The phosphoric acid was determined by the molybdic acid method:—

·1875 gramme gave		
·0225	gramme	H_2O
·068	,,	$Ca''O$ (weighed caustic)
·042	,,	$Al_2'''O_3$
·089	,,	$Mg''_2P_2O_7$

* Chiefly silica, which I have assumed to be an intruding material, perhaps without sufficient reasons Yet, while the lime, alumina, and phosphoric anhydride exhibit a definite and constant ratio, the silica does not.

These results lead to the following oxygen ratio of base, acid, and water—

6 : 5 : 3

This is the ratio of dufrenite, and of several other native phosphates.

The experimental percentages are as follow :—

$Ca''O$	36·27
Al'''_2O_3	22·40
P_2O_5	30·36
H_2O	12·00
	101·03

These numbers lead to the formula

$$3Ca''O.P_2O_5.Al'''_2O_3 + 3H_2O,$$

which may be thus abbreviated by the adoption of the lower atomic weights and the mineralogical notation—

$$\dot{C}a_3\dot{P} + \dot{A}l_2 3H.$$

The theoretical percentages demanded by this formula are

$Ca''O$	35·97
Al'''_2O_3	22·06
P_2O_5	30·41
H_2O	11·56
	100·00

The only known mineral phosphate resembling the present species is one examined by Damour in 1853, and believed by him to be a hydrous phosphate of alumina and lime. I am not aware that any quantitative analytical result was obtained by Damour, save a determination of water in the mineral. This amounted to 12·7 per cent. Damour's phosphate was found in the diamond sands of Bahia. It occurred in rounded pebbles. Its hardness exceeded that of glass, and in other physical characters it differed widely from the species now described. Our present mineral is from Tavistock, Devonshire: the specimen in the British Museum is placed with wavellite.

III. *Hydrated Plumbo-cupric Arsenate.*

A Cornish specimen, supposed to be arsenate of copper, was submitted to special examination on account of its high density and strong resinous lustre. Qualitative analysis at once revealed the presence of lead. Although many mineral species are double compounds of copper and lead (caledonite, chileite, linarite, vauquelinite, &c.), yet I am not aware of any double arsenate of lead and copper, definite and constant in composition, having been yet discovered and described. The following details concerning such a compound may therefore not be without interest. I may state at the outset that I propose the name "Bayldonite" for this species, in honour of my friend and former colleague, Dr. John Bayldon.

Bayldonite occurs in minute mammillary concretions, having a drusy surface: the structure of the masses is often somewhat reticulated after the manner occasionally observed in certain travertines.

The fracture is slightly conchoidal, uneven. Translucent on the edges. The lustre is more or less distinctly resinous. Colour grass-green to blackish-green. Colour of the powder siskin-green to apple-green.

The hardness of Bayldonite is about 4·5.

Its specific gravity is 5·35.

It gives in the oxidising flame a blue borax bead. On ignition it gives off water only, and becomes black. On charcoal it readily fuses to a black bead, and then suddenly gives off fumes of arsenic with deflagration: a metallic bead (a hard white alloy of lead and copper) remains on the charcoal. Nitric acid is the best solvent for Bayldonite: by the aid of heat and subsequent addition of hot water, the finely powdered mineral dissolves, though with some difficulty; a residue, chiefly consisting of quartz and amounting to from 1 to 3 per cent., remaining unacted on.

The analyses were made as follows:—The excess of acid in the nitric acid solution of the mineral having been removed, the lead was precipitated by means of sulphuric acid and the subsequent addition of a little alcohol. From the filtrate from the sulphate of lead the alcohol was removed by evaporation to dryness. To the nitric acid solution of this residue ammonia was added in excess, and then magnesia-mixture: the precipitate was collected

on a weighed filter. In the filtrate, after suitable treatment, the copper was determined. In one case the arsenic acid was precipitated by molybdate of ammonia. The following are the analytical results:—

I.	·617	gramme	gave ·249	$Pb''SO_4$.
I.	·617	,,	,, ·193	$Cu''O$.
I.	·617	,,	,, ·026	H_2O.
II.	·62	,,	,, ·2565	$Pb''SO_4$.
II.	·62	,,	,, ·189	$Cu''O$.
II.	·62	,,	,, ·3225	$Mg''_2(NH_4)_22AsO_4 + H_2O$.
II.	·62	,,	,, ·031	H_2O.
III.	·773	,,	,, ·32	$Pb''SO_4$.
III.	·773	,,	,, ·409	$Mg_2(NH_4)_22AsO_4 + H_2O$.
III.	·773	,,	,, ·038	H_2O.
IV.	1·05	,,	,, ·044	H_2O.

The above numbers correspond to the following percentages:—

	I.	II.	III.	IV.
$Pb''O$	29·64	30·45	30·31	—
$Cu''O$	31·28	30·48	—	—
*As_2O_5	—	31·49	32·02	—
H_2O	4·21	5·00	4·92	4·19
		97·42		

The mean experimental percentages are therefore as follow:—

$Pb''O$	30·13
$Cu''O$	30·88
As_2O_5	31·76
H_2O	4·58
Ferric oxide, lime and loss..	2·65
	100·00

These numbers lead to the oxygen ratio, between base, acid, and water, of

4 : 5 : 2 nearly,

* In Analysis II. the ammonio-magnesian arsenate was specially examined for phosphoric acid. It was dissolved in HCl, the arsenic removed by hyposulphite of sodium, and the phosphoric acid precipitated as ammonio-magnesian phosphate; ·013 grm. of the pyrophosphate was thus obtained, corresponding to ·76 p. c. P_2O_5.

very similar to that of konichalcite and of pseudolibethenite,—perhaps identical with it. The formula deduced from the analysis is—

$$Pb''O.3Cu''O.As_2O_5 + 2H_2O,$$

which may be arranged thus :—

$$Pb''O,2Cu''O,As_2O_5 + Cu''H_2O_2 + aq.$$

or tricupric arsenate in which $\frac{1}{3}$ of the copper is replaced by lead; together with 1 atom of cupric hydrate and 1 atom of water. One reason for disallowing the expression

$$3Cu''O.As_2O_5 + Pb''O + 2aq.$$

is the evident decomposition of the substance on heating, with change of colour: the cupric hydrate, outside the arsenate itself, becoming anhydrous and black. Olivenite, however, in which it is believed there likewise exists 1 atom of hydrate of copper, becomes olive-green only on gentle ignition, and at a bright red heat assumes an emerald tint, no separation of cupric oxide being apparent. The present species differs in amount of water from olivenite, or I should have thought it to be that species in which 1 atom of copper had been replaced by lead. All the so-called varieties of olivenite, even the light "wood" arsenate, contain no more than 3·38 per cent. of water, corresponding exactly to the formula—

$$3Cu''O.As_2O_5 + Cu''H_2O_2.$$

The theoretical values demanded by the formula $Pb''O,2Cu''O,As_2O_5 + Cu''H_2O_2 + aq.$ are as follow :—

$Pb''O$	223·0	30·65
$3Cu''O$	238·6	32·79
As_2O_5	230·0	31·61
$2H_2O$	36·0	4·94
	727·6	100·00

It should be stated that in some analyses not here recorded the percentage of $Pb''O$ in the mineral was as high as 33·1. It is also worthy of note that almost all the determinations of water are below the percentage demanded by the accepted formula,

though they agree much more nearly with it than with any other simple expression.

Minute traces of chlorine and sulphuric acid have been found in some specimens of Bayldonite, in addition to the ferric oxide and lime, to which allusion has been already made.

I am indebted to Mr. Talling for this mineral species also.

XLII.—*On a new series of bodies in which Nitrogen is substituted for Hydrogen.*

By Peter Griess.

I.

For a number of years I have been engaged in investigating a peculiar class of nitrogen-compounds, which are obtained by the action of nitrous acid upon amido-compounds, the latter exchanging 3 atoms of their hydrogen for 1 atom of nitrogen from the nitrous acid.

I have up to the present time prepared a large number of these compounds, many of which I have already minutely described.* They are all distinguished by remarkable physical and chemical properties, especially by their tendency to explode with great violence when heated, and by the facility with which they exchange 2 atoms of nitrogen for other atomic groups, thereby frequently forming substitution-products of great interest. It is on account of this property that I have given the name of "diazo-compounds" to this class of bodies. I purpose in this and in some future communications to give a short sketch of the most important representatives of this class.

Diazodinitrophenol.

On passing a current of nitrous acid gas into an alcoholic solution of picramic acid, $C_6H_3(NO_2)(NH_2)O$, the originally red colour of the solution is observed to change to yellow, a rise in the temperature taking place at the same time. Meanwhile the whole of the nitrous acid is absorbed, whilst scarcely a trace of nitrogen is evolved. After the gas has been passing some time, a few yellow plates of diazodinitrophenol

* Ann. Ch. Pharm. c. 201; cxvii. 1; cxxi. 257. Phil. Trans., Part III, p. 667.

appear in the solution. They rapidly increase, and are deposited in the form of a lustrous crystalline mass. The process is finished as soon as the separation of crystals has ceased. The new substance when separated from the mother-liquor and recrystallised several times from boiling alcohol, is sufficiently pure for analysis. Another, though less convenient method of preparing diazodinitrophenol consists in dissolving picramic acid in nitric acid, and passing a current of binoxide of nitrogen into the solution. The solution, after being concentrated, yields with water a yellow precipitate, which is purified by recrystallisation from alcohol. Analysis led to the formula—

$$C_6H_2N_4O_5 = C_6H_2(NO_2)_2N_2O.$$

The formation of the new body takes place according to the following equation:—

$$\underset{\text{Picramic acid.}}{C_6H_5N_3O_5} + NHO_2 = \underset{\text{Diazodinitrophenol.}}{C_6H_2N_4O_5} + 2H_2O.$$

Diazodinitrophenol crystallises in golden-yellow plates of great beauty; it is difficultly soluble in alcohol and in ether, insoluble in water. It has a slight bitter taste, and explodes at a high temperature with great violence. It has no action on litmus or turmeric.

Ordinary nitric acid, sulphuric acid, and hydrochloric acid dissolve diazodinitrophenol without alteration; it evinces, on the whole, very great stability in the presence of acids. It may be boiled for days with fuming nitric acid, without undergoing the slightest alteration, even fuming sulphuric acid destroys it only at a high temperature. It is not attacked by dry chlorine. It is, however, decomposed on boiling for a considerable time with water. In addition to a small quantity of a resinous substance, a reddish-brown powder is obtained, which, though soluble in alcohol, ether, and caustic potash, cannot be obtained in crystals.

Diazodinitrophenol suffers a most remarkable decomposition under the influence of alcohol, in the presence of alkalis. On treating an alcoholic solution of it with a solution of carbonate of potassium, and gently heating the mixture, an evolution of gas ensues, whilst the colour of the originally yellow solution turns to red. As soon as the evolution of gas has ceased, the excess of alcohol is distilled off; the residue on cooling yields brownish-red

needle-shaped crystals of a potassium-salt, which, when recrystallised and treated in solution with dilute nitric acid, give light yellow plates easily soluble in alcohol.

This acid, for the most part, forms beautifully crystallised salts. Its properties, as well as the analysis, establish its identity with dinitrophenylic acid $C_6H_4(NO_2)_2O$.

The gas evolved during the decomposition of diazodinitrophenol by alcoholic potassa was proved by analysis to consist of pure nitrogen. The reaction takes place thus:—

$$\underset{\text{Diazodinitrophenol.}}{C_6H_2N_4O_5} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Dinitrophenylic acid.}}{C_6H_4(NO_2)_2O} + N_2 + \underset{\text{Aldehyde.}}{C_2H_4O.}*$$

I have determined the quantity of nitrogen evolved. 0·237 grm. substance gave 26·6 c. c. nitrogen at 0°, and 760 m. m. Bar. weighing 0·0334 grm. = 14·1 p. c. The preceding equation requires 13·3 p. c.

If diazodinitrophenol is boiled with a solution of aqueous potash another compound is obtained, which may possibly be oxydinitrophenylic acid.

Diazodinitrophenol, as already stated, is prepared by dissolving picramic acid in alcohol, and passing nitrous acid into the solution. If this proceeding be reversed, and the picramic acid be added to the alcohol previously saturated with nitrous acid and slightly warmed, a different reaction takes place. In this case a powerful evolution of gas ensues, whilst not a trace of diazodinitrophenol separates. When the reaction is over, the alcohol is distilled off, and the residue treated with water, a copious separation of crystals is obtained, which, on further purification, exhibit all the properties of dinitrophenylic acid.

It may, however, be noticed that in the preparation of diazodinitrophenol traces of dinitrophenylic acid are invariably formed.

Diazonitrophenol.

This compound is obtained by treating amidonitrophenylic acid $(C_6H_4(NO_2)(NH_2)O)$† with nitrous acid. It is, however, not advisable to employ an alcoholic solution of the acid, on account of

* The aldehyde was recognised by its peculiar odour.

† Gerhardt and Laurent, when describing this acid under the name of dinitrodiphenamic acid (Compt. Rend. des trav. de Chim., 1849, p. 468) assigned to it a formula double of that given above. I, however, think that the simpler formula is preferable.

the solubility of the diazonitrophenol in that liquid. From an ethereal solution, on the other hand, it separates completely as soon as the nitrous acid has passed through for a short time, whilst not a trace of nitrogen is evolved. The product when only washed a few times with ether is already fit for analysis. Numbers were obtained leading to the formula

$$C_6H_3(NO_2)N_2O.$$

Diazonitrophenol, when separating from the ethereal solution, appears as a brownish-yellow granular mass. It is very soluble in alcohol. On allowing the solution to evaporate spontaneously it is deposited in the same granular form. Even in hot water it is very difficultly soluble, being at the same time partly decomposed, and converted into an amorphous red powder. The filtered solution on cooling deposits the greater part of the substance in the form of small yellow crystals, which appear as thick prisms under the microscope. These crystals have a sweetish bitter taste, and when ground yield a light yellow powder, which, on exposure to light, assumes a dark red colour. Diazonitrophenol has no action on vegetal colours. The dry compound cannot be heated up to 100°, as at that temperature it is decomposed with a violent explosion, exerting at the same time a destructive power which can only be compared to that of fulminate of mercury.

Diazonitrophenol is but slightly soluble in ether, but cold hydrochloric acid and sulphuric acid readily dissolve it without decomposition; addition of water precipitates it as a reddish flocculent mass. Ebullition with fuming nitric acid converts it into a substance which, on the addition of water, separates as a curdy precipitate.

Diazonitrochlorophenol $C_6H_2(NO_2)ClN_2O$.

This substance is obtained by acting with nitrous acid upon an alcoholic solution of amido-nitrochlorophenylic acid ($C_6H_3Cl(NO_2)(NH_2)O$*). It may be prepared with equal facility by first saturating the alcohol with nitrous acid and then introducing the amido-acid. In both cases it is separated from the mother-liquor by filtration and recrystallised from alcohol, from which it is obtained on cooling in large brownish-red prismatic crystals of perfect purity. When dried at 100°, they gave on analysis numbers corresponding with the formula given above.

* Ann. Ch. Pharm. cix. 290.

Diazonitrochlorophenol possesses great power of crystallisation. From alcohol, in which it is but slightly soluble, it separates in brownish-red prismatic crystals. It is also difficultly soluble in hot water and in ether. From the former it crystallises in greenish golden yellow plates; from the latter in needles, which are often grouped in sheaves. When dissolved in ordinary sulphuric acid and then treated with water, it is obtained in thread-like crystals which frequently attain the length of three inches.

In its other points, it exhibits great analogy with the preceding compounds. It is dissolved by acids without decomposition; it forms a yellow powder which acquires a red colour on exposure to the light. It is, however, capable of bearing a much higher temperature than diazonitrophenol, and may be dried at 100° without danger; at a higher temperature it also deflagrates with violence.

As far as my view of the rational constitution of the substances described in the preceding pages is concerned, I think I have already clearly expressed it by the names which I have chosen for them. I refer them to the type of phenylic acid, and assume that in these bodies two atoms of hydrogen are replaced by two monoatomic atoms of nitrogen, or perhaps better by one double atom.

$C_6H_2(NO_2)_2(N_2)''O$.	$C_6H_3(NO_2)(N_2)''O$.	$C_6H_2(NO_2)Cl(N_2)''O$.
Diazodinitrophenol.	Diazonitrophenol.	Diazonitrochlorophenol.

This view is supported by the transformation which diazodinitrophenol undergoes when boiled with alcoholic potash, in which case the two atoms of nitrogen are, in fact, exchanged for two atoms of hydrogen. It is self-evident that this view does not stand in opposition to the fact that these diazo-compounds arise through the substitution of three atoms of hydrogen by one atom of nitrogen, especially if we bear in mind the analogous reaction which takes place when nitrous acid acts upon ammonia:

$$NH_3 + NHO_2 = (N_2)'' + 2H_2O.$$

One glance at this equation shows that in this case also three atoms of hydrogen are replaced by one atom of nitrogen, and that the molecule of nitrogen produced is equivalent to two atoms of hydrogen.

XLIII.—*On the Decay of Gutta-percha and Caoutchouc.**

By Prof. William Allen Miller, M.D., F.R.S.

The inquiries to which this investigation has given rise have extended over many months, and have included a large number of analyses, but the results obtained may be stated in a small compass, as they are very definite. I have examined numerous samples of gutta-percha cables both injured and sound, which have been in use for several years, and I find in all cases that the deteriorated portions have undergone chemical change, and that change consists in a process of *oxidation*.

Whatever retards or prevents this oxidation, retards or prevents the decay of the gutta-percha, some of the specimens which I examined being as good as new, though they had been manufactured and used electrically for years; whilst others in a few months had become brittle, rotten, and unserviceable. As the general result of these inquiries, I find that whenever the gutta-percha has been completely submerged in water no injurious change has occurred, sea-water appearing to be eminently adapted to the preservation of the gutta-percha. On the other hand, alternate exposure to moisture and dryness, particularly if at the same time the sun's light has access, is rapidly destructive of the gutta-percha, rendering it brittle, friable, and resinous in aspect, and in chemical properties. A gradual absorption of oxygen takes place, and the gutta-percha slowly increases in weight, becoming at the same time proportionately soluble in alcohol, and in dilute solutions of the alkalies. In every instance, however, some portion of the gutta remained unchanged in composition.

My experiments have also been extended to the prolonged action of air, moisture, and light, upon india-rubber, and here also I find that these agents effect analogous changes, though somewhat less rapidly.

* A paper on this subject by Mr. Spiller having recently appeared, it has been thought that the Fellows might be interested in an official report made five years ago to the Joint Committee appointed by the Lords of the Committee of Privy Council for Trade and the Atlantic Telegraph Company, to inquire into the Construction of Submarine Telegraph Cables.—[Ed.]

The caoutchouc, however, instead of becoming brittle, is converted into a glutinous mass, losing its elasticity, increasing in weight to a certain extent, and becoming partially soluble in alcohol and diluted alkaline liquids.

These deductions are made from the examination of a number of samples supplied to me partly by Captain Galton and Mr. L. Clark, including specimens of coated telegraphic wires suspended in air, specimens of submarine cables, specimens of wires sunk in the soil under various conditions, besides experiments instituted by myself upon the action of various agents upon gutta-percha, and they include the results of an extended and well-contrived series of experiments made at the works of the Electric Telegraph Company under the direction of Mr. L. Clark.

I will here subjoin an abstract of the principal experimental details, and for the convenience of reference will arrange them under the following distinct heads:—

1st. Experiments upon pure gutta-percha.
2nd. Experiments upon commercial gutta-percha.
3rd. Experiments upon submerged cables.
4th. Experiments upon decayed and damaged cables exposed in air and underground under various circumstances.
5th. Experiments upon caoutchouc.
6th. Experiments upon other compounds.

1. *Experiments on Pure Gutta.*

Pure gutta differs in some of its properties from the commercial gutta. I found on examining the whitest samples purified by Dr. Cattell, that it formed a porous, milk-white mass, wholly soluble in benzol, in ether, in bisulphide of carbon, and in the ordinary solvents of gutta-percha. It is a perfectly pure hydrocarbon probably containing $C_{20}H_{30}$. I found it to consist of—

	Found.		$C^{20}H^{30}$.
Carbon	88·96	or	88·88
Hydrogen.....	11·04		11·12
	100·00		100·00

When exposed to a temperature of 212° it softens, but does not liquefy; it loses a trace of moisture, and then gradually absorbs

oxygen, becoming brown, brittle, and resinous in appearance. In one specimen the increase in weight amounted to 4·45 per cent. The oxidized portion is insoluble in benzol, which when digested on the brown mass dissolves out a quantity of unaltered gutta, which had been protected from oxidation by the coating of resin.

This resinous mass when thus purified was found to have been produced from the gutta-percha by simple absorption of oxygen, the gutta having in one experiment absorbed more than a fourth of its weight of oxygen from the atmosphere.

2. *Chemical Experiments on Commercial Gutta-percha.*

The gutta-percha of commerce is not a pure proximate vegetable principle, but it consists chiefly of a hydrocarbon, which may for brevity be termed *pure gutta*, or simply gutta, mixed with a product of its oxidation which is in the form of a soft resin, amounting to about 15 per cent. in the best commercial samples.

The following is the composition of a piece of ordinary good commercial gutta-percha, taken from a piece of new cable supplied to me by Mr. L. Clark :—

Pure gutta	79·70
Soft resin	15·10
Vegetable fibre	2·18
Moisture	2·50
Ash	0·52
	100·00

The moisture reported in this analysis is mechanically diffused through the mass of the gutta-percha, and seems to have some influence upon its pliability and toughness. 100 parts of the commercial sample when dried at 212° till it ceased to lose weight, deducting the ashes, contained—

Carbon	84·66
Hydrogen	11·15
Oxygen	4·19
	100·00

This gutta-percha softens and liquefies by a heat of 212°. It is soluble, with the exception of a few flocculi of fibrous matter, in benzol, in bisulphide of carbon, and in ether. Alcohol dissolves none of the pure gutta, but extracts a portion of the soft resin. This resin is an oxidised compound, probably in a transitional condition to a higher stage of oxidation. I found it to consist of—

Carbon	76·15
Hydrogen	11·16
Oxygen	12·69
	100·00

The true gutta was extracted nearly pure from this sample by dissolving it in benzol, filtering and adding alcohol, when a coagulum of pure gutta was obtained, which was found to consist of—

Carbon	87·22
Hydrogen	12·04
Oxygen	0·74
	100·00

The presence of the small quantity of oxygen in this case was due to a little of the resin which still adhered to the precipitated mass of gutta.

Commercial gutta-percha may be preserved for months, and even years, with little change, either in water or in air, provided light be excluded. This I have found from my own experiments, and the results which I have myself obtained are confirmed by experiments made by Mr. Clark. The following are some of the most important of these experiments:—500 grs. of thin sheet gutta were exposed under various conditions at the end of last October at the Electric Cable Works. The various samples were examined on the 2nd of July of this present year (1860).

1. In netting exposed to sun and rain in open air.
2. In a bottle open to the air and light, but excluded from rain.
3. In a bottle open to the air, but excluded from light.
4. In fresh water, open to air and light.
5. In fresh water, open to air excluded from light.
6. In fresh water, excluded from air and light.

7. In sea water, exposed to air and light.
8. In sea water, excluded from light but exposed to air.
9. In sea water, excluding both light and air.

The specimens 4, 5, 6, 7, 8, and 9 were wholly unaltered, with the exception of a slight increase in weight, due to the absorption of water, which they lost again after exposure to the air for an hour or two. The tenacity and structure of the material did not appear to have undergone the slightest change.

No. 2, which had been folded up and introduced into a bottle, the mouth of which was open and inverted, had increased in weight from 500 grs. to 524·5 grs., or about 5 per cent., owing to absorption of oxygen from the air. The outer layers of the sheet, where exposed to light, were brittle and resinous in appearance, but the inner portion, which had been screened from light by the outer folds, was but little altered in texture or appearance.

On examining chemically a portion of the most brittle part, I found a large portion of it to have lost the composition of gutta, and to have become converted into a matter soluble in alcohol, 55 per cent. of the mass being in fact transformed into the resin already spoken of.

The sample No. 3, which had been kept in the dark, had experienced little or no change. It had only increased 2·5 grains in weight, or 0·5 per cent.; and when treated with alcohol gave up 7·4 per cent. of resinous matter to it.

These results agree with those which I made upon gutta-percha which had been exposed to the light of day for the shorter period of two months. This specimen had become quite brittle, had increased in weight 3·6 per cent., and yielded 21·5 per cent. of resinous matter soluble in alcohol; whilst a piece of the same sheet kept in the dark had undergone no sensible change.

Samples of sheet gutta-percha were also subjected in November last to the action of the following liquids, and exposed to diffused daylight :—

A. Boiled linseed oil.	C. Stockholm tar.
B. Linseed oil not boiled.	D. Coal tar.

When examined on the 4th of August, 1860, or at the end of nine months, these liquids were found not to have exerted any perceptible solvent action upon the gutta, which retained its texture and tenacity in all those portions which had been fairly submerged in the liquid, and protected from the light and atmos-

pheric air; but in those portions which had projected into the atmospheric air contained in the jar, where it was also exposed to the effects of diffused daylight, the texture had become rotten, and the material more or less brittle and resinous.

All the liquids above mentioned are calculated to exclude oxygen from the gutta-percha, and thus they are enabled to exert a preservative influence upon it, without, however, in any degree softening or dissolving its texture. Hence they are likely to be highly valuable agents in coating the insulating material.

3. *Experiments on Submarine Cables.*

I have examined several specimens of cable from different lines which have been submerged for periods of time varying from a few weeks to seven years. In no case where the cable has been completely and continuously submerged have I found any sensible deterioration in the quality of the gutta-percha.

No. 1. Holyhead Irish cable (from Captain Galton), taken up in February, 1859, after seven years' submergence.

No. 2, *a*. *b*. *c*. Three specimens from the Dutch line, from Orfordness to Schevening (Mr. L. Clark), submerged five years, raised in August, 1859.

This cable was enclosed in a coating of galvanized iron wire, and contained a single wire of copper in gutta, bound round with hemp and tape soaked in boiled linseed oil, tallow, and Stockholm tar.

a. External coating of galvanized wire, not damaged by corrosion. This sample had been buried on the Dutch coast to a small depth in sand.

b. and *c*. Outer galvanized wire much corroded, but the gutta-percha quite sound. The gutta-percha wire had in each of these samples been exposed to the air, out of the metallic casing, for some months, and consequently was drier than the sample *a*, taken from its metallic coating just before it was analysed.

No. 3. Cable off Portland (Captain Galton); down for seven months; composed of seven thin copper wires twisted into a strand covered with tar, then coated with gutta-percha, without any metallic protecting envelope.

No. 4. Cable from line between Candia and Alexandria (Captain Galton). Construction similar to the last; it showed superficial

erosions of the gutta-percha after submergence for a few weeks; but the composition of the gutta was unchanged.

No. 5. New gutta-percha covered wire (Mr. L. Clark); never used.

The only chemical difference perceptible in these different specimens was in the quantity of water mechanically retained in each.

100 parts of each contained :—

	1.	2.			3.	4.	5.
		a.	*b.*	*c.*			
Water	0·84	3·36	1·75	1·49	4·8	0·96	2·50
Ash	1·05	..	..	0·76	3·52	0·75	0·50

4. *Experiments upon damaged Cables suspended in Air or placed underground.*

Of damaged cables I have had various specimens for examination.

1 to 6. Six samples, described by Mr. Saward in his evidence before the Committee, January 12, 1860.

1. Buried in chalky or gravelly soil, coated with a white, friable crust of altered gutta-percha. This was very brittle, and contained 35 per cent. of resin; this resin contained 17 per cent. of oxygen combined with a hydrocarbon of the same composition as pure gutta.

2. Was in soil exposed to leakage of gas-pipes, and also was resinous and brittle, but less so than No. 1.

3. Was described as pulpy when raised, as if fermenting; taken from ground into which drainage from oak trees or posts occurred. When forwarded to me it was hard and tough, the copper wire within was slightly corroded and adhered to the gutta-percha, the channel around the wire lined with a pale brown powder. This powder contained traces of copper. It appears to consist of gutta-percha, as it was almost wholly soluble in benzol, and was insoluble in alcohol. The material in this case seemed to have undergone comparatively little permanent change, although so very different in appearance from ordinary gutta-percha, when it was taken up. It fused below 212°. It had been painted with some pigment

containing lead, and on burning left an ash amounting to 1·87 per cent.

4. Not very brittle, taken from iron pipes.

5. Exposed to a dry heat near a baker's oven; coated with red lead.

6. Exposed to a dry heat (exact source not indicated). This was extremely brittle, could be powdered without difficulty, and was almost converted into a resinous substance. It fused below 212°, it left 1·03 per cent. of ash when burnt, and appeared to have been coated with some pigment.

In all these samples those which were most brittle contained the oxidized resinous body in largest proportion. This resinous substance varied somewhat in the proportion of oxygen which it contained in the different samples, but presented the same general properties. It was soluble in cold alcohol, and still more largely in boiling alcohol; was insoluble in ether, and but sparingly in benzol; diluted alkaline leys dissolved it with facility, and the solution coagulated on the addition of an acid in excess.

7 and 8. Samples of gutta-percha covered wire taken from a tunnel in the Stour valley, placed in the tunnel in 1850 (Mr. L. Clark). One portion of this, A, was comparatively little injured; the other, B, was brittle and rotten. This sample had been coated with some pigment containing lead.

It would be useless to cite in detail the various analyses which I have made of these several samples, or to give the numbers obtained for the proportion of moisture, ash, and resin which they contained, or to quote the proportions of carbon, hydrogen, and oxygen ascertained to exist in the altered portion, as contrasted with the unchanged portion, present in each sample.

It may be stated generally, that wherever the proportion of resin was greatest, the sample of gutta exhibited the greatest degree of brittleness; and this brittleness was always found to be most marked in the specimens which had experienced the greatest degree of oxidation; and further, that these changes appeared to occur most rapidly and decidedly in those points where the gutta-percha was alternately wet and dry.

5. *Experiments on Caoutchouc.*

The caoutchouc of commerce is, like gutta, not a pure vegetable principle, and consists of a hydrocarbon of definite composition,

mixed with a small quantity of resin, the amount of which varies in different specimens.

The following are the results of my analysis of a sample of pure unmanufactured Para rubber, compared with a sample of good sheet masticated or manufactured rubber.

	Virgin.	Masticated.
Pure caoutchouc	96·6	96·64
Moisture.....	1·3	0·82
Resin	1·8	2·06
Ash.....	0·3	0·48
	100·0	100·00

Or, deducting moisture and ash, its elementary composition gave—

	Virgin.	Masticated.
Carbon	85·82	85·53
Hydrogen.....	11·11	12·06
Oxygen	3·07	2·41
	100·00	100·00

Caoutchouc, like gutta-percha, is, as already stated, liable to deterioration, by exposure to the action of oxygen in the presence of solar light, but the gum is less rapidly injured if exposed to their influence in the native state, than if it has been previously masticated. When subjected to the action of air excluded from light, it does not experience any marked change, even during very long periods. It is, however, important to observe that the masticated rubber is much more porous than the unmanufactured caoutchouc. When immersed in water, caoutchouc absorbs a much larger quantity of this liquid than gutta-percha, and the masticated much more than the unmanufactured or virgin rubber. I subjoin the results of my examination of some samples submitted to experiment by Mr. L. Clark.

A.—*Virgin Para Rubber, Finest Quality.*

500 grains of this was exposed in each experiment, in the form of a narrow tape-like strip of rubber, which had been stretched while hot and suddenly cooled. It was of a very pale brown colour. The various samples were submitted to experiment at the

end of October, 1859, and were examined nine months afterwards (August 4th, 1860).

No. 1, which had been exposed in netting, in the open air, to sun and rain, had become blackened and rotten, but was neither sticky nor crumbled, had increased in weight 34·5 grains or 7 per cent.

No. 2 was exposed in the air and light, but kept dry in a bottle placed mouth downwards; it had increased in weight 14 grains, or 2·8 per cent., by absorption of oxygen, and had become brown, soft, and sticky, especially in the parts most exposed to light. It gave up 11·81 per cent. of an oxidized, soft, and viscous resin to alcohol. The annexed analysis will give an idea of the composition of the resin thus formed:—

Carbon	67·23
Hydrogen	9·54
Oxygen	23·23
	100·00

The proportion of oxygen differs a little in different samples.

No. 3, which was exposed to diffused light in fresh water in an open bottle, had become white and opaque from the absorption of moisture, and had increased 86 grains, or 17 per cent., but it had experienced no other alteration in chemical properties, and when dried resumed its original characters.

No. 4, exposed in sea-water in an open bottle to diffused light, had absorbed 3·6 per cent. of its weight of water, but was only a little altered in appearance, not in chemical composition.

B.—*Masticated Rubber, Sheet, Best Quality.*

A similar series of experiments was made simultaneously upon masticated sheet caoutchouc.

No. 1, exposed to sun and rain, had collected into a sticky mass, which had lost its tenacity and elasticity.

No. 2, in the inverted bottle exposed to diffused light and air, had increased in weight 8 grains, or 1·6 per cent., and had collected into a lump, which was viscous, and had lost its elasticity, especially in the parts most exposed to the action of light. When treated with alcohol it was found to yield 12·64 per cent. of its weight of

resinous matter to this solvent. These changes were in marked contrast to No. 3, which was kept in a glass bottle in the dark for the same period, but exposed to the air freely. It had increased in weight only 0·6 per cent., did not show any sign of alteration in tenacity or elasticity, and yielded to alcohol 2·0 per cent. of resin only.

No. 4, a sheet of the same rubber immersed in fresh water, open to the air and diffused light, had increased 87 per cent. by absorption of water, that is to say, it had nearly doubled its weight. It had become white, opaque, slimy, and sticky when pressed, and allowed water to be squeezed out by pressure. It lost weight rapidly by drying when exposed to the air.

No. 5, similar to the last, but exposed in sea-water. It was slightly opaque and slimy, but had increased only 5 per cent. in weight by absorption. A second sample, in sea-water in a closed bottle, emitted a smell of sulphuretted hydrogen, and had gained 5·6 per cent. in weight by absorption. Its elasticity and tenacity were not impaired. The gradual permeability of masticated caoutchouc to water was further strikingly shown by enclosing a quantity of acetate of potash in bags made of sheet rubber and accurately sealed. They were then immersed in water, and at the end of nine months the salt in each of the bags was found to have become liquefied by the water which it had absorbed, and the bags had in each case gained in weight several grains.

C.—*A similar Series of Experiments was made with Sheet Rubber, vulcanized.*

1. The sheet exposed in the netting to the sun and rain had lost 2 per cent. in weight; it was scarcely less tenacious than at first.

2. A similar sheet in fresh water absorbed 19 per cent., but was not otherwise altered.

3. A similar sheet in sea-water was rather more slimy, and had only gained 1·6 per cent. in weight.

Each of the three substances, viz., natural, masticated, and vulcanized rubber were submitted to the action of the following solvents for nine months:—

A. Boiled linseed oil.
B. Unboiled linseed oil.
C. Stockholm tar.

The *virgin rubber* had resisted the action of the solvents almost perfectly, retaining its toughness, excepting in those parts which were above the surface of the liquid and exposed to light. In the tar this rubber had contracted spontaneously, but was still strong and elastic.

The *masticated rubber* was in each instance greatly swollen and gelatinized, and indeed in the case of the unboiled oil was completely dissolved.

The *vulcanized rubber* had also lost its tenacity, and had become swollen and gelatinous, but retained its form and a certain degree of elasticity.

A sample of india-rubber cable (from Captain Galton), which contained six strands of copper wire, each coated with rubber, then bound round with tape and again with rubber, had experienced a singular change, having become, *where in contact with the wire*, quite glutinous and sticky. This change, however, did not progress in the specimen which I kept for some months in my room, but the viscosity on the contrary gradually diminished.*

6. *Experiments on other Substances.*

An insulating mixture composed of gutta-percha, shellac, and powdered glass or clay, known as "Wray's Compound" (from Captain Galton), was also submitted to experiment.

Heated to 212°, it softened, but retained its shape. It lost by drying 0·5 per cent. of moisture, and when burnt left 22 per cent. of a white ash, chiefly silicate of alumina. This compound absorbs water but sparingly. 500 grains left in fresh water for six months increased 7·5 grains in weight, or 1·5 per cent., and a similar increase in weight occurred in another experiment where *sea*-water was used.

Sample of Gutta-Percha Cable (from Captain Galton) vulcanized by Mackintosh's Patent.

The wire was found to be blackened on its surface from the action of the sulphur, owing to the formation of sulphide of copper, and traces of copper were found in the gutta-percha covering.

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* The quantity of viscous matter was too small to admit of satisfactory analysis, I ascertained, however, that no copper was present in the viscous mass, and that the wire was not corroded. I could not determine whether grease was present in small quantity, as was not unlikely.

XLIV.—*On the Absorption of Vapours by Charcoal.*

By John Hunter, M.A.

University of California Library

Priestley and Scheele were aware of the property which charcoal possesses of absorbing different gases. Guyton Morveau, in 1782, stated that he had seen a piece of charcoal absorb all the gas contained in a jar, and Lowitz recognised the deodorising and decolorising powers of charcoal. Count Morozzo was the first who attempted to obtain an accurate measurement of the volume of gas absorbed, but his observations are of comparatively little value, as he does not mention the nature of the charcoal, and appears to have allowed it to come into contact with the air before being introduced into the gas. In 1799, shortly after the experiments of Morozzo were published, Messrs. Rouppe and Van Norden made a number of observations on the same subject; the method adopted by them, however, was also defective, and had the additional disadvantage, that the absorptions were determined over water instead of mercury. In 1812, Th. de Saussure communicated to the Geneva Society his celebrated memoir on the absorption of the gases by different bodies, and although the subject appears to be deserving of further investigation, it has scarcely attracted any attention since that time.*

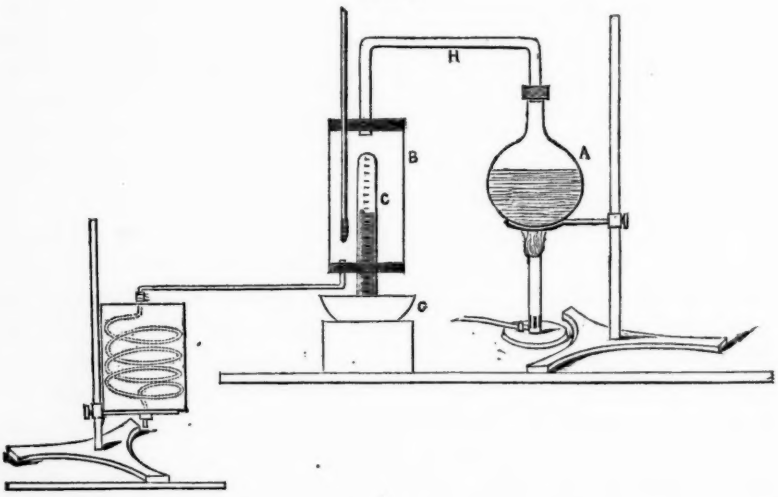
In 1863, I published in the Philosophical Magazine the results of a series of experiments on the absorption of gases by different varieties of charcoal. My principal object in commencing this inquiry was to obtain greater absorptions than any previously observed, by using charcoals formed from very dense and hard woods. The charcoals prepared from logwood and ebony exceed boxwood charcoal in the power of condensing gases within their pores, the first absorbing 111·3 times its volume of ammonia. On further investigation I found that charcoal made from the shell of the cocoa-nut had by far the greatest absorbing power. It is very dense and brittle, the pores are quite invisible, and when broken the edges present a semi-metallic lustre. It absorbs scarcely any mercury during cooling, increasing only seven per cent. in weight. Having examined the absorption of a large

* Some important experiments on the absorption of gases by charcoal were published by Dr. R. Angus Smith, in 1863 (Proc. Roy. Soc. xii, 424).—Ed.

number of the gases, I extended the inquiry to the absorption of aqueous vapour, and the vapours of different liquids, principally with a view of ascertaining whether any relation existed between their absorption and chemical composition. The present short paper contains the results of these experiments.

The apparatus employed is represented in Fig. 1. The liquid to be converted into vapour is contained in a small glass bulb, which is introduced into the graduated tube C, standing in the mercurial bath G. This tube is surrounded by an outer glass vessel B, which is connected with a flask, A, by a bent tube, H. Through an opening in the cover of the outer vessel, B, a thermometer is introduced for the purpose of determining the temperature of the vapour. The graduated tube passes through an opening in the lower part of B, and close to it is a pipe for the purpose of conveying the vapour to a small worm surrounded by cold water where it is condensed.

Fig. 1



In performing an experiment, a quantity of the liquid requisite to give the required temperature is placed in the flask A. The graduated tube C, having been carefully dried and filled with warm mercury to avoid any risk of moisture being present, is inverted in the bath, and a small glass capsule containing the liquid whose vapour we wish to absorb, is introduced into the tube. The flask A is then connected with the outer vessel B, and the tube

leading from the latter to the condenser is attached. On heating the liquid in the flask to its boiling point, the vapour passes over, fills B, and is then condensed. The contents of the little capsule in C enter into ebullition, and the vapour occupies a number of divisions, which are read off when the temperature of the external vapour remains nearly constant. The height of the barometer and difference in level of the mercury in the tube and in the bath are also noted. The charcoal having been heated to redness out of contact with air, is plunged, while in a state of incandescence, under the mercury and then introduced into the tube. When the absorption is completed, the residual volume is read off. The tube C could be moved up and down so as to adjust the mercury in it, to about the same level during the entire experiment. For the purpose of obtaining high temperatures, oil of turpentine and fousel oil were introduced into the flask A; the former gave a temperature of from 158° to 161° C., and the latter from 127° to 131° C.

A remarkable fact connected with the absorption of vapours by charcoal is, that it teminates in a much shorter time than in the case of the permanent gases, rarely, if ever, exceeding an hour. Methylic alcohol is more largely absorbed than the other vapours examined at temperatures of 90°, 100°, and 127° C., exceeding the absorption of ordinary alcohol; yet at 159° C. the order is reversed, methylic alcohol being absorbed to the amount of 60·5 volumes, and ordinary alcohol 83·4, by one volume of cocoa-nut charcoal, showing that the absorptions do not decrease in the same ratio. In all cases the absorptions became less as the temperature rose, and it is interesting to observe the great change in ammonia and carbonic acid, which are absorbed respectively, at 0° C., 171·7 and 67·7 by one volume of cocoa-nut charcoal, and, at 127° C., only 21·9 and 16·6. In several cases, as ether, chloroform, the absorption changes slowly as the temperature rises. Glacial acetic acid was used in determining the absorption of acetic acid vapour.

In the following tables, V represents the number of volumes of the vapour absorbed by one volume of cocoa-nut charcoal, at the temperature and pressure at which the experiment is performed. T and $\grave{T}$ are the initial and final temperatures, P and $\grave{P}$ the pressures, deduced by subtracting the difference in level from the height of the barometer.

These experiments were performed in the laboratory of the Queen's College, Belfast.

WATER.

	V	T	$\dot{T}$	P	$\dot{P}$
	49·8	130·0	133·0	554·7	549·2
	42·2	121·0	120·0	548·3	541·8
	42·8	122·2	121·0	586·3	580·3
	38·5	123·5	125·0	628·0	624·0
	45·8	130·0	131·0	695·8	687·8
	41·0	127·0	131·0	663·4	650·4
	45·8	129·0	132·0	673·1	672·6
	44·5	125·0	128·5	684·3	681·1
Mean ..	43·8	127·3	127·7	629·1	623·5
	23·4	159·0	159·5	695·7	694·2
	23·5	159·3	159·5	698·8	697·3
	25·5	158·2	159·2	687·7	696·2
	22·2	159·0	159·0	692·5	698·0
	26·8	158·2	159·3	691·2	692·2
	21·0	157·5	158·0	688·3	688·3
Mean ..	23·7	158·5	159·1	692·3	694·3

BISULPHIDE OF CARBON.

	V	T	$\dot{T}$	P	$\dot{P}$
	93·4	158·5	159·0	691·8	693·3
	90·0	157·0	156·0	661·8	668·8
	90·8	157·7	159·0	650·4	644·4
	88·7	157·2	160·0	641·4	645·8
	93·1	155·0	158·0	645 2	645·7
Mean ..	91·2	157·1	158·4	658·1	658·6
	117·8	100·0	100·0	669·7	671·7
	117·1	100·0	100·0	672·7	674·2
	116·6	100·0	100·0	671·2	667 7
Mean ..	117·2	100·0	100·0	671·0	671·2

METHYLIC ALCOHOL.

	V	T	$\dot{T}$	P	$\dot{P}$
	56·7	159·0	159·4	684·2	683·2
	60·2	158·5	159·2	689·7	687·2
	61·3	158·0	159·5	686·0	683·5
	63·9	158·0	159·0	681·3	680·5
Mean ..	60·5	158·4	159·2	685·0	683·8
	123·3	127·0	131·5	686·0	656·7
	127·2	126·3	129·0	679·1	660·1
	123·4	126·1	126·0	678·7	672·0
Mean ..	126·6	126·5	128·8	681·3	662·9
	148·9	100·0	100·0	656·2	640·2
	146·8	100·0	100·0	660·8	653·8
	156·3	100·0	100·0	672·8	661·8
Mean ..	150·7	100·0	100·0	663·3	651·6
	151·2	91·0	91·0	716·7	714·2
	154·1	91·0	91·0	713·0	714·5
	154·9	90·0	90·0	693·2	697·2
Mean ..	153·4	90·6	90·6	707·6	708·6

FOUSEL OIL.

	V		T	$\dot{T}$		P	$\dot{P}$
	31·5	....	156·5	158·5	....	663·7	657·2
	26·0	....	159·0	159·8	....	695·6	699·8
	28·6	....	159·0	160·0	....	697·1	704·1
	25·1	....	159·5	160·5	....	699·2	700·4
Mean ..	27·8	....	158·5	159·7	....	688·9	690·4

ALCOHOL.

	V		T	$\dot{T}$		P	$\dot{P}$
	87·8	....	157·5	159·3	....	662·4	662·4
	80·8	....	157·7	161·5	....	665·5	659·5
	82·0	....	157·8	160·7	....	671·8	668·8
	84·0	....	157·0	158·0	....	661·2	661·7
Mean ..	83·4	....	157·5	159·9	....	665·2	663·1
	111·8	....	126·2	129·7	....	641·1	622·3
	111·0	....	126·0	125·0	....	691·6	680·8
	109·8	....	126·0	127·0	....	665·6	653·8
	110·8	....	126·0	126·2	....	660·2	622·3
Mean ..	110·8	....	126·1	126·9	....	664·6	644·3
	140·0	....	100·0	100·0	....	660·3	656·8
	137·2	....	100·0	100·0	....	649·2	647·2
	146·2	....	100·0	100·0	....	652·0	653·0
Mean ..	141·1	....	100·0	100·0	....	653·8	652·3
	144·7	....	90·0	90·0	....	700·7	703·7
	142·3	....	90·0	90·0	....	702·0	706·0
	134·8	....	88·0	88·0	....	708·5	710·3
	161·8	....	90·0	90·0	....	717·8	720·8
Mean ..	145·8	....	89·5	89·5	....	707·2	710·2

BENZOL.

	V		T	$\dot{T}$		P	$\dot{P}$
	63·0	....	126·8	129·8	....	661·3	656·3
	61·8	....	129·7	130·8	....	658·4	619·4
	53·7	....	127·0	130·8	....	662·6	647·6
	50·4	....	126·5	129·8	....	660·3	659·2
Mean ..	58·7	....	127·7	130·3	....	660·6	645·6

ETHER.

	V		T	$\dot{T}$		P	$\dot{P}$
	53·8	....	158·0	160·0	....	686·2	682·2
	54·0	....	159·0	160·5	....	686·0	685·0
	55·4	....	157·8	159·0	....	687·7	683·7
Mean ..	54·3	....	158·3	159·8	....	686·6	683·6
	70·6	....	127·3	127·5	....	658·0	656·5
	67·0	....	128·5	131·0	....	667·8	662·3
	67·3	....	126·4	126·2	....	667·6	663·6
Mean ..	68·3	....	127·4	128·2	....	664·4	660·8
	82·8	....	100·0	100·0	....	643·4	643·9
	80·7	....	100·0	100·0	....	654·2	640·2
	92·9	....	100·0	100·0	....	649·7	644·7
	91·6	....	100·0	100·0	....	645·3	644·8
Mean ..	87·0	....	100·0	100·0	....	648·1	643·4

CHLOROFORM.

	V	T	$\dot{T}$	P	$\dot{P}$
	20·5	158·0	159·3	653·8	655·8
	22·3	157·5	161·0	649·8	649·8
	20·2	157·8	159·0	676·2	685·2
	20·2	158·0	159·0	650·3	650·3
Mean ..	20·8	157·8	159·5	657·5	660·2
	28·0	100·0	100·0	658·3	656·3
	32·0	100·0	100·0	641·7	641·2
	28·6	100·0	100·0	640·2	644·7
Mean ..	29·5	100·0	100·0	646·7	650·7

ACETIC ACID.

	V	T	$\dot{T}$	P	$\dot{P}$
	82·9	158·0	160·0	692·0	683·0
	86·3	158·0	159·0	667·1	948·6
	80·1	158·7	159·2	688·3	689·8
	83·1	157·6	159·0	690·2	683·2
Mean ..	83·1	158·1	159·3	684·4	675·9

AMMONIA.

	V	T	$\dot{T}$	P	$\dot{P}$
	18·6	127·0	129·7	641·3	645·8
	21·7	121·0	119·8	671·4	663·9
	25·5	129·1	131·0	670·5	658·5
Mean ..	21·9	125·7	126·8	661·0	655·4

CARBONIC ACID.

	V	T	$\dot{T}$	P	$\dot{P}$
	16·4	125·0	125·0	666·4	670·4
	15·7	126·2	128·0	700·7	703·2
	17·7	127·3	127·0	682·1	687·1
Mean ..	16·6	126·2	126·7	683·0	686·9

XLV.— *On Caprylic and Œnanthylic Alcohols.*

By Ernest T. Chapman.

By the distillation of castor-oil with an excess of alkali, Bouis obtained a substance which he himself regarded at one time as caprylic, at another as œnanthylic alcohol. This substance has been the subject of numerous investigations, but the results obtained do not coincide. Nevertheless, all chemists who have

worked on this subject obtain a compound boiling at about 178°, but they differ as to the composition and vapour-density of this compound. In other words, a substance having one of the chief characteristics of homogeneity, a constant boiling point, and obtained from one source by one method, is found by different chemists to differ in composition.

This unsatisfactory state of affairs it was which in the first instance attracted my attention to the subject, and induced me to re-investigate it. And though my investigations have not in any way served to explain this anomaly, they have, I think, placed it beyond doubt that, under some circumstances, both caprylic and œnanthylic alcohols are present in the distillate, and that the substance boiling at 178° is not always œnanthylic alcohol.

In order to obtain the alcohol, the castor-oil was saponified with solution of soda, and the soap formed was separated by means of salt, and transferred to a metal retort. About a third of its weight of caustic soda was then added, and the mixture dried, by heating it until the smell of the alcohol was produced; the head of the retort was then fixed on, and the distillation proceeded with. The distillate consisted of water and an oily substance; the latter was agitated with a concentrated solution of bisulphite of soda, and allowed to stand for 24 hours; the resulting mass was squeezed in a cloth to separate the solid from the liquid portions, and the oily part of the latter was removed and dried over caustic potash, and then distilled off. The distillate was then fractionally distilled; it began to boil below 100°, but the greater part came over between 170° and 180°, after which the thermometer rose steadily and evenly, without showing any signs of becoming stationary, up to the boiling point of mercury, beyond which temperature I considered it unnecessary to continue the distillation. [N.B.—Those portions which passed over above 250° had no action on potassium, even when boiled upon it. Pentachloride of phosphorus also was without action upon them.]

That part of the fluid which distilled between 178—181° was redistilled, when by far the greater portion boiled constantly at 179°. Two combustions of the substance were made, and gave the following results:—

Combustion.	Substance.	CO_2	H_2O
A	·469 gave	1·267	·5959
B	·502 „	1.357	·6301

	Theory.	Found. A	Found. B	Average.
C_8	73·845	73·67	73·72	73·695
H_{18}	13·846	14·11	14·07	14·090
O	12·309			
	100·000			

A determination of the vapour-density of this substance was made. The balloon employed, in this as in all other vapour-density determinations throughout this paper, was filled with hydrogen.

The results were—

Temperature of the air	14·5°
Barometer	749 mill.
Temp. of bath at moment of sealing ..	209°
Increase in weight of globe . ..	0·8680
Cubic contents of globe	283 c.c.
Residual gas	0
Weight of hydrogen in globe	0·0238
Weight of vapour in globe	0.8918
Volume of vapour at 0° and 760 mill. ..	160·2

Therefore sp. gr. 62·0 (H = 1), or 4·305 (air = 1).

Suspecting that there might be some hydrocarbon present with a similar boiling point to that of the alcohol, I treated the substance with iodine and phosphorus, with the view of obtaining a compound of the alcohol-radical, which should have a boiling point considerably higher than the alcohol. On fractionally distilling the product, the greater portion of the distillate was found to be a liquid, heavier than water, boiling at 212° with slight decomposition. This was collected separately, and digested at a moderate warmth with caustic potash, whereby the alcohol was reproduced, but with a slightly higher boiling point, viz., 182°. A little of this alcohol was converted into chloride of capryl by treatment with pentachloride of phosphorus: the chloride thus formed boiled at 175°, the temperature which has ordinarily been stated to be its boiling point. It, like the iodide, was then converted into an alcohol with the same boiling point as that obtained from the iodide. I therefore assumed this substance to be pure, at least to be free from hydrocarbons. A combustion of it gave the following results:—

Substance.	CO_2	H_2O
·5955	1·3383	·6283

Theory.		Found.
C_8 ..	73·84	73·66
H_{18} ..	13·84	14·08
O....	12·32	

This determination, it will be seen, differs but little from the preceding determinations, nothwithstanding the difference of boiling point.

A determination of the vapour-density of this substance gave the following results :—

Temperature of air	14°
Barometer	751 mill.
Temperature of bath at sealing	204°
Increase of weight in globe	0·9846
Cubic contents of globe	315 c.c.
Residual gas	0
Weight of hydrogen in globe	0·0266
Weight of vapour in globe	1·0112
Volume of vapour at 0° and 760 mm. ..	172

Therefore sp. gr. 65·4 (H. = 1) or 4·54 (air = 1).

The substance employed in the above experiments was quite free from iodine; its boiling point was perfectly constant; its smell differed from that of the crude product, and its taste was far less burning.

Bromide of capryl was prepared both from the crude alcohol and from the substance purified as above. The two liquids were perfectly similar; but the crude product gave a much smaller proportion of the bromide than the purified alcohol, that is to say, in fractionally distilling the products, much more liquid boiling below 190° was obtained from the crude alcohol than from the purified substance. If distilled from an oil-bath, the temperature of which was not allowed to exceed 191°, it boiled without decomposition. A portion of it was digested with alcoholic ammonia, in a sealed tube, at a temperature of 100° for twenty-four hours; the tube was opened, and the contents distilled with solution of potash; the distillate was mixed with a fresh portion of bromide, and again digested at the same temperature. (A much higher alcohol, in which chloride of capryl, and, as I supposed, chloride

temperature cannot be employed, as decomposition is very apt to take place.) The product was evaporated to dryness on the water-bath, dissolved in water, potash added, and the strong smelling oily liquid which separated, was again digested with a fresh portion of bromide. The product was again evaporated on the water-bath, then introduced into a retort, with a concentrated solution of potash, and distilled by passing a current of steam through it. The water having been separated from the base, a portion of the latter was dissolved in alcohol, acidulated with hydrochloric acid, and precipitated with bichloride of platinum. The precipitate formed immediately and seemed to be amorphous. It was filtered off, and its percentage of platinum determined. The following figures were obtained.—

Quantity of Substance.	Platinum found.	Percentage.
·4457	·0814	18·27
·4985	·0910	18·26
·5167	·0941	18·22

Average percentage 18·25. Theoretical 18·17.

An analysis of the base itself was made.

Substance. CO_2 H_2O. N.

·5445 gave 1·6259 and ·7135 and ·0216

	Theory.	Found.
C_{24} ..	81·59	81·44
H_{51} ..	14·44	14·56
N ..	3·97	3·89
	100·00	99·89

These numbers can, I think, leave little doubt that the substance in question is *Tri-caprylamine*, and that, therefore, the distillate obtained from castor-oil and excess of alkali *contains* caprylic alcohol. I think I am in a position to show that it also contains œnanthylic alcohol.

That portion of the original alcohol which boiled between 170°—178° was submitted to careful fractional distillation, but without obtaining a definite boiling-point. This I supposed was due to the substance in question being a mixture of caprylic and œnanthylic alcohols, and, perhaps, also of hydrocarbon. To remove the latter, the substance was treated with pentachloride of phosphorus and distilled. The distillate was agitated with weak

of œnanthyl are nearly insoluble, and the oily matters which were not dissolved, were separated, dried on chloride of calcium, distilled off, and fractionally distilled. They began to boil at 166°, about half coming over between 166° and 170°. The thermometer then rose to 175°, at which temperature the remainder distilled. I did not examine the latter portion further, but have no doubt that it was chloride of caprol. The part which came over at the lower boiling point, was subjected to repeated fractional distillation. The greater portion of it passed over between 168° and 170°. It was then digested with potash, and distilled off, when it was found to boil at about 173°. One combustion of this substance was made. It yielded numbers which would not quite coincide with those of œnanthylic alcohol, but were sufficiently near to make it probable that the substance was simply contaminated with a little caprylic alcohol.

Substance.	CO_2	H_2O.
·4845 gave	1·2948 and	·6236

	Theory.	Found.
C_7 ..	72·42	72·88
H_{16}..	13·79	14·30
O ..	13·79	
	100·00	

This substance was converted into bromide. This bromide is much more easily decomposed than the corresponding capryl compound. It cannot be distilled without liberation of bromine. By treatment similar to that which furnished tri-caprylamine, it was made to yield a base, possessed of very similar properties, and which also gave a precipitate with bichloride of platinum. Two determinations of the percentage of platinum in the platinum-salt gave :—

A. substance taken ·4625 gave ·0948 of platinum.
B. „ „ ·5975 „ ·1237

A. equals 20·49 p.c.
B. equals 20·70 p.c.
} average 20·595 per cent.

The amount of substance was not sufficient to make an analysis; but these determinations, taken in conjunction with the analysis of the alcohol, seem to me to show that the substance in hand is a mixture of caprylic and œnanthylic alcohols. The percentage of platinum in the tricaprylamine salt would be 18·17; in the tri-œnanthylamine salt, 23·5.

During my investigations of capryl compounds, I obtained caprylic ether. It was produced by the action of bromide of capryl on potasso-caprylic alcohol. The latter substance was obtained by acting on caprylic alcohol with potassium. When on adding more of the metal, no further action was observed, the resulting substance was washed by decantation with ether, pressed between blotting-paper, and dried in vacuo. Equivalent quantities of this substance and of the bromide were digested together in a sealed tube at 100° for about an hour. The tube was then opened and the fluid contents distilled off. The distillate was found to boil at 53°; only a few drops had a higher boiling point, and they contained bromine.

One combustion of the substance was made.

Substance.	CO_2	H_2O.
·5255	1·5197	·6740

		Theory.	Found.
C_8H_{17} } O	C	79·34	78·87
C_8H_{17} }	H	14·05	14·25
	O	6·61	
		100·00	

Metallic zinc decomposes both the iodide and bromide of capryl, when they are digested with it. Iodide and bromide of zinc and a hydro-carbon are the products.

In order to compare the alcohol obtained from castor-oil with that formed synthetically from petroleums, I acted on that portion of the Canadian petroleum which distils from 115° to 120°, in a manner analogous to that described by Pelouze and Cahours,* and, like them, obtained a compound having the composition of chloride of capryl; from this I formed both the acetate and the alcohol. Of this latter substance the following vapour-densities and analyses were made. The substance seemed to me to be in all respects analogous to the caprylic alcohol obtained from castor-oil; it boils at 183°.

* Ann. Ch. Phys. [4], I, 53.

Determination A.

Temperature of air	16°
Barometer	745 mm.
Temperature of bath at moment of sealing	214°
Contents of globe	364 c.c.
Weight of hydrogen contained by globe	0·0303
Residual gas	0
Increase in weight of globe	1·1336
Weight of vapour which globe contained	1·1639
Volume of vapour at 760 and 0°	200 c.c.

Therefore sp. gr. 64·8 (H = 1) or 4·5 (air = 1).

Determination B.

Temperature of air	17°
Barometer	743 mm.
Temperature of bath	221°
Contents of globe	362 c.c.
Weight of hydrogen in globe	0·0299
Residual gas	0.
Increase of weight in globe	1·0978
Weight of vapour in globe	1·1277
Volume of vapour at 760 and 0°	195 c.c.

Therefore sp. gr. 64·3 (H = 1) or 4465 (air = 1).

Two combustions of the substance were also made :—

	Substance.		CO_2		H_2O.
A	·5642	gave	1·5255	and	7104
B	·4846	„	1·3113	„	6110

	Theory.	Found. A	Found. B	Average.
C_8	73·84	73·73	73·79	73·760
H_{18}	13·84	13·99	13·96	13·975
O	12·32			
	100·00			

I conclude from the above that the decomposition of the castor-oil soap or ricinolate of potash is not so simple as it is ordinarily represented to be; that in addition to the alcohols mentioned in

the above paper, many other substances are present; and, finally, that I have not met with any fact which militates against the assumption that the compound $C_8H_{18}O$ from castor oil is identical with that obtained from petroleum.

Since writing the above I have made another distillation of castor oil and alkali (the seventh which I have made), and for the first time find that almost all the products combine with bisulphite of soda. I merely mention this as showing that the composition of the distillate is not by any means constant.

XLVI.—*On a New Class of Organic Compounds in which Hydrogen is replaced by Nitrogen.*

By Peter Griess.

II.

The interesting substances described in the first part of this paper (p. 268), obtained by the action of nitrous acid upon some of the amido-acids of the phenyl group, induced me also to study the action of nitrous acid upon similarly constituted bodies from other groups. I have thus obtained a number of remarkable products, of which, for the present, I will describe only those which may be referred to amido-acids belonging to the family of aromatic acids.

Here also the reaction takes place in a similar manner to that previously described yet a considerable difference is observed in the fact that the atoms of nitrous acid and amido-acid which act upon each other, are not equal in number, but that one atom of nitrous acid acts upon two atoms of the amido-acid.

Diazodinitrophenol is formed according to the equation—

$$\underset{\text{Picramic acid.}}{C_6H_5N_3O_5} + NHO_2 = \underset{\text{Diazodinitrophenol.}}{C_6H_2N_4O_5} + 2H_2O.$$

On the other hand, the action of nitrous acid upon amido-benzoic acid, for instance, is expressed by the equation—

$$\underset{\text{Amidobenzoic acid.}}{2C_7H_7NO_2} + NHO_2 = \underset{\text{New compound.}}{C_{14}H_{11}N_3O_4} + 2H_2O.$$

The compounds which arise, according to the last equation, possess all the characteristic properties of the bodies described in the first paper. They exhibit, moreover, many peculiarities which are partly founded on their complicated composition, and are particularly manifested by a larger number of products of decomposition. I refrain from treating minutely of these relations at present, and content myself with giving first a special description of the preparation and properties of one of these substances.

Diazo-Amidobenzoic Acid.

This substance is prepared by passing a current of nitrous acid into a cold, saturated, alcoholic solution of pure amidobenzoic acid $C_7H_5(H_2N)O_2$. After the gas has been passing for a few moments, the wine-red colour disappears, and immediately, or after a short time the new body separates in the form of an orange-yellow crystalline powder. The heat generated must be moderated by cooling with water. When the quantity of the precipitate no longer increases, the operation is discontinued, and the new substance collected on a filter, in order to separate it from the mother-liquor. Frequent washing with warm alcohol renders it perfectly pure.

An aqueous solution of amidobenzoic acid, when submitted to the action of nitrous acid, also yields the new body. This mode of preparation, however, is scarcely to be recommended, as the resulting product is never so pure, or so beautiful as that obtained by the first method.

The following process, on the other hand, is very advantageous, especially when working with small quantities. It is based on the observation that the ethers of nitrous acid exert the same action upon amidobenzoic acid as the free nitrous acid itself. On mixing an alcoholic solution of nitrous ether (which, for this purpose, may be prepared simply by saturating cold alcohol with nitrous acid) with an alcoholic solution of amidobenzoic acid, scarcely any alteration takes place in the cold; but on gently heating the mixture up to about 30° its colour at once changes from red to yellow, whilst the new body is precipitated in abundance, generally in the form of microscopic needles, which are rendered perfectly pure by washing with alcohol.

Pure nitrite of ethyl, as well as nitrite of amyl, produce exactly the same results.

Analysis of the acid led to the formula

$$C_{14}H_{11}N_3O_4.$$

The following equation explains the formation of this substance, for which I have proposed the name of *Diazo-amidobenzoic Acid.*

$$\underset{\text{Amidobenzoic acid.}}{2C_7H_7NO_2} + NHO_2 = \underset{\text{New acid.}}{C_{14}H_{11}N_3O_4} + 2H_2O.$$

In fact, the operation may be conducted in such a manner that the quantity obtained corresponds almost exactly with that required by theory. As a rule, however, other products arise in variable proportions, the formation of which is chiefly due to an excess of nitrous acid. In a subsequent part of this paper I shall again refer to this circumstance.

Diazo-amidobenzoic acid is obtained in small crystals of a beautiful orange-yellow colour. They appear as small prisms when seen under the microscope. It is inodorous and tasteless, almost insoluble in water, alcohol, ether, bisulphide of carbon and chloroform, and consequently cannot well be recrystallised from these solvents. Mineral acids dissolve it readily, especially on the application of heat, but it cannot be separated from them again without decomposition. When dissolved in a solution of potash or ammonia, and then neutralised with an acid, the new substance is precipitated all unaltered in the form of a yellow gelatinous mass.

It can be dried at 100° without decomposition. At 180° it deflagrates, in consequence of a rapid evolution of gas.

Although diazo-amidobenzoic acid is a somewhat weak acid, it, nevertheless, completely saturates the strongest alkalis, and expels carbonic acid from their carbonates.

Salts of Diazo-amidobenzoic Acid.—Although diazo-amidobenzoic acid always combines with two atoms of metal, yet it cannot be viewed as a bibasic acid, if by that term is understood an acid containing a diatomic radical, and capable of forming two series of salts—acid and neutral—as it fulfils neither of these conditions. It assumes more the character of a compound acid.

Diazo-amidobenzoate of Potassium $C_{14}H_9K_2N_3O_4$. In order to

obtain this salt a quantity of the acid is introduced into a large excess of a concentrated aqueous solution of carbonate of potassium, which has been heated up to 80°. On cooling a quantity of extraordinarily small needle-shaped crystals separate, they are of a yellowish-white colour, and when floating in the mother-liquor give rise to a most vivid fluorescence.

Diazo-amidobenzoate of Ammonium, $C_{14}H_9(NH_4)_2N_3O_4$, crystallises in microscopic needles, which, when in aqueous solution, are readily decomposed by heat.

Diazo-amidobenzoate of Sodium, $C_{14}H_9Na_2N_3O_4$, resembles the potassium-salt in all respects.

Diazo-amidobenzoate of Barium, $C_{14}H_9Ba_2N_3O_4$, is obtained in the form of a yellowish-white crystalline precipitate on treating the potassium-salt with a solution of chloride of barium. In order to purify it for analysis it is well washed with water, and dried over sulphuric acid. This salt is nearly insoluble in water, quite insoluble in alcohol and in ether. When heated on platinum-foil, it deflagrates.

Diazo-amidobenzoate of Magnesium crystallises in yellow needles, easily soluble in water.

Diazo-amidobenzoate of Silver, $C_{14}H_9Ag_2N_3O_4$, falls as a greenish-yellow mass on treating a neutral solution of the acid in ammonia with nitrate of silver. It is purified from the mother-liquor by repeated washing with water. When dried it appears as a yellow powder, equally insoluble in water, alcohol, and ether. It remains unaltered at 100°. At a higher temperature it deflagrates with violence, thus rendering it impossible to determine the silver by heating. The analysis is, however, easily performed by dissolving the salt in dilute nitric acid, and precipitating the silver with hydrochloric acid.

The *calcium-salt* is a yellowish-white precipitate, resembling the barium salt.

A solution of the potassium salt gives a yellowish-green precipitate with chloride of mercury, and a yellow precipitate with chloride of iron.

Diazo-amidobenzoate of copper, when dry, appears as a green, amorphous powder. The zinc salt is yellow, amorphous, insoluble in water.

Diazo-amidobenzoate of Ethyl, $C_{14}H_9(C_2H_5)_2N_3O_4$. This compound is prepared by passing a stream of nitrous acid through an alcoholic solution of amidobenzoic ether, $C_7H_4(H_2N)(C_2H_5)O_2$.

Yellow crystals soon appear in the solution. They rapidly increase, and soon cause the whole liquid to solidify. The crystals are collected on a filter, and separated from the mother-liquor by washing with cold alcohol. One recrystallisation from boiling alcohol yields this body in magnificent hair-like needles of an almost golden-yellow colour. They are insoluble in water, but dissolve readily in alcohol and in ether. They fuse at 144° (uncorr.), but do not resolidify on cooling until the lapse of several days. At a higher temperature they are decomposed with evolution of nitrogen.

The deportment of the ether towards dilute acids appears to be that of a weak base, dissolving in them, although with difficulty, and being reprecipitated on addition of ammonia. It would, however, be difficult to obtain definite compounds, as it is scarcely possible to prevent the acids from causing a further decomposition. The formation of the ether takes place according to the following equation :—

$$\underset{\text{Amidobenzoic ether.}}{2C_7H_4(H_2N)(C_2H_5)O_2} + NHO = \underset{\text{New ether.}}{C_{14}H_9(C_2H_5)_2N_3O_4} + 2H_2O.$$

Diazo-amidobenzoate of Methyl, $C_{14}H_9(CH_3)N_3O_4$, is prepared by acting upon an ethereal solution of amidobenzoate of methyl with nitrous acid. The new ether separates in small crystalline globules or in short lance-shaped yellow crystals.

It melts at 160° (uncorr.) and on resolidifying exhibits the same peculiarity as the preceding compound, which it also resembles in all other respects.

Products of Decomposition of Diazo-amidobenzoic Acid.

Action of the Haloid Acids upon Diazo-amidobenzoic Acid.—On treating this acid with strong hydrochloric acid, no reaction is observed at the ordinary temperature, but on gentle heating, an evolution of nitrogen takes place, the original acid disappears whilst a crystalline body is produced. It is separated by filtration from the mother-liquor, from which a second white crystalline substance is obtained on evaporation. The first body is purified by dissolving in a large quantity of boiling water and decolorising with animal charcoal. On cooling, a copious crystallisation of delicate white needles is obtained, which are rendered perfectly pure by a second crystallisation. They are easily soluble in

alcohol and in ether, with difficulty in cold, more readily in hot water; they are so volatile that they cannot be dried in the water-bath without loss.

This substance is a well-defined acid. An analysis gave numbers leading to the formula of chlorobenzoic acid: $C_7H_5ClO_2$.

Limpricht and Uslar were the first to point out that chlorobenzoic acid produced by the decomposition of chlorinated chloride of benzoyl with water is not identical with the substance of the same composition obtained by distilling salicylic acid with pentachloride of phosphorus and treating the resulting distillate with water. The latter acid, discovered by Chiozza, was, in a more recent research by Kolbe and Lautemann,* distinguished as a peculiar acid, and called by them chlorosalicylic acid.

Both the crystalline form and the melting point (152° uncorr.) of the compound prepared according to my method, decided me in declaring it to be identical with the chlorobenzoic acid of Limpricht and Uslar.

I have mentioned another product of decomposition, which is found dissolved in the hydrochloric mother-liquor from which the chlorobenzoic acid had been separated. This second body is obtained in a state of perfect purity by evaporating the hydrochloric acid, dissolving the residue in alcohol, precipitating with ether, and several times recrystallising the precipitate. The substance thus obtained corresponds perfectly, in its crystalline form, its sweetish-sour taste, and its beautifully crystallised platinum-salt, with hydrochlorate of amidobenzoic acid. Its identity was further established by a chlorine determination.

The following equation may serve to elucidate this transformation:—

$$C_{14}H_{11}N_3O_4 + 2HCl = C_7H_5ClO_2 + C_7H_5(H_2N)O_2.HCl + N_2.$$

The quantities of the products of decomposition obtained correspond with this assumption, as shown by the following determination of the quantity of the nitrogen evolved. The substance was introduced into a long-necked flask from which the air had been expelled by a stream of carbonic acid, and treated with a sufficient quantity of hydrochloric acid. The gases evolved during ebullition were conducted into a graduated glass tube filled with

* Ann. Ch. Pharm. cxv., 183.

potassa solution. The gases remaining in the flask were driven into the graduated tube by a fresh current of carbonic acid. After absorption of the carbonic acid the residue was found to be pure nitrogen.

1·06 grm. of substance dried at 100° and decomposed with hydrochloric acid, gave 75 c.c. nitrogen at 0°, and 760 mm. bar. = 8·9 p.c. The equation given above requires 9·9 p.c. These facts lend a powerful support to the view that diazo-amidobenzoic acid is a compound acid of diazobenzoic acid and amidobenzoic acid, viz. :—

$$\left\{ \begin{array}{l} C_7H_4N_2O_2 \\ C_7H_5(H_2N)O_2. \end{array} \right\}$$

By taking this formula, the decomposition by hydrochloric acid is at once explained. In the first stage of the reaction, the original compound is split up into its two constituents, amidobenzoic acid and diazobenzoic acid, and in the second the diazobenzoic acid, which possesses but little stability, exchanges its two atoms of nitrogen for hydrochloric acid, thus forming chlorobenzoic acid. This view of the rational formula of diazo-amidobenzoic acid is still further confirmed by the following experiments :—

On heating the dry substance to 180° or 190° in an apparatus similar to that above described, a violent reaction suddenly ensues, which, if much substance has been employed, assumes the character of a weak explosion. Torrents of nitrogen are evolved and are collected in the graduated tube. The neck of the flask containing the substance becomes filled with a sublimate of white crystals, whilst a fused substance remains at the bottom. The gas collected in the graduated tube is pure nitrogen, whilst the crystals, by their sweetish taste and their deportment with nitrous acid, with which they yield the original substance*, are at once recognised as amidobenzoic acid.

The fused substance remaining at the bottom of the flask possesses the character of an acid ; it is insoluble in water, but easily soluble in alcohol. I have not analysed it ; the mode of its formation, however, can leave scarcely a doubt of its composition

* The deportment of an alcoholic solution of amidobenzoic acid with nitrous acid offers a simple method for the detection of the latter. Even traces of nitrous acid contained in an alcoholic or ethereal liquid may easily be recognised by the formation of diazo-amidobenzoic acid.

being $C_7H_4O_2$. The reaction would consequently take place thus:—

$$\underset{\text{Diazo-amidobenzoic acid.}}{C_{14}H_{11}N_3O_4} = \underset{\text{Amido-benzoic acid.}}{C_7H_7NO_2} + \underset{\text{New acid.}}{C_7H_4O_2} + N_2.$$

The quantity of nitrogen actually obtained corresponded with that required in the preceding equation.

0·447 grm. substance gave 33·9 c.c. nitrogen at 0° and 760 m.m. bar. = 9·53 p.c.; theory 9·8 p.c. This experiment shows that the same quantity (viz., $\frac{2}{3}$ of the total amount) of nitrogen which is expelled from diazo-amidobenzoic acid by hydrochloric acid, is also set free by the action of heat alone.

A totally different result is obtained on attempting to determine the amount of nitrogen by ignition with soda-lime. Here, actually, only the one equivalent of nitrogen contained in the double acid in the form of amide is converted into ammonia, the other two atoms of nitrogen escaping as such.

0·4785 grm. gave 0·3495 grm. platinum-salt, corresponding to 4·6 p.c. of nitrogen. The quantity of nitrogen in the form of amide contained in diazo-amidobenzoic acid is 4·9 p.c.

Diazo-amidobenzoic acid must therefore be added to those substances which cannot be analysed with correct results by the method of Will and Varrentrapp.

Action of Hydriodic acid upon Diazo-amidobenzoic acid.—On heating diazo-amidobenzoic acid with aqueous hydriodic acid the same phenomena are observed as those produced by the action of hydrochloric acid. Two new bodies are formed, one of which separates as a reddish-coloured crystalline mass, whilst the other is retained in solution by the acid mother-liquor. If the first be dissolved in very dilute alcohol, and digested with a little animal charcoal, the filtered solution on cooling deposits a copious crop of white or slightly-reddish crystals, which are rendered fit for analysis by a second crystallisation.

The new substance appears in the form of delicate plates, extremely soluble in alcohol and in ether, but difficultly soluble in water. Analysis proved them to be *iodobenzoic acid* $C_7H_5IO_2$.

The mother-liquor of this acid contains hydriodate of amidobenzoic acid, which, when purified, forms white needles of sweetish-sour taste, easily soluble in water, difficultly soluble in alcohol, insoluble in ether.

The formation of the two products just described, is accomplished in exactly the same manner as that of chlorobenzoic and amidobenzoic acid :—

$$C_{14}H_{11}N_3O_4 + HI = C_7H_5IO_2 + C_7H_7NO_2.$$

It appears thus, that the formation of chlorobenzoic and of iodobenzoic acid is based upon a new and most peculiar mode of substitution, the peculiarity of which consists in the replacement of two atoms of nitrogen by one atom of hydrochloric or hydriodic acid. Doubtless similar results will be obtained with other hydrogen acids, and will thus give rise to many new and interesting compounds.

Not only these acids, however, but also their ethers decompose the double acid, with evolution of nitrogen.

I have not had sufficient time at my disposal to submit the products thus obtained to a more minute examination.

Action of Chlorine, Bromine, and Iodine upon Diazo-amidobenzoic Acid.

Chlorine, bromine, and iodine individually act upon diazo-amidobenzoic acid. The degree of energy with which this action takes place, as well as the formation of distinct products, is determined, not only by the nature of the element, but also in an eminent degree by the form in which the element is employed, whether in the anhydrous state or in the presence of water or alcohol.

The addition of anhydrous bromine to the double acid gives rise to an explosive decomposition; torrents of nitrogen and hydrobromic acid are evolved, whilst the residue is changed to a brownish easily fusible resin. This resin is nearly insoluble in water, easily soluble in alcohol and in alkaline liquids; acids reprecipitate it from the latter without alteration. It evidently consists of a mixture of brominated acids, from which it is scarcely possible to isolate a definite compound by crystallisation. When the resin is submitted to dry distillation in a retort, a brominated derivative of benzoic acid sublimes, whilst the residue is charred, with evolution of hydrobromic acid vapours.

Finely divided diazo-amidobenzoic acid suspended in water and submitted to the action of bromine, yields products differing in a

marked manner from those produced by the action of anhydrous bromine. For although the resin above-mentioned is formed in considerable quantity, yet chiefly crystallisable acids are produced, the separation of which, however, is still attended with difficulty.

If we bear in mind that in the action of bromine upon water we produce hydrobromic acid and oxygen, and, assuming the simplest case, that both these, in combination with an excess of bromine, act only upon the first constituent of diazo-amidobenzoic acid, viz., upon the atomic group $C_7H_4N_2O_2$, it is obvious that at least the two following series of acids may be formed :—

$C_7H_5BrO_2$	$C_7H_5BrO_3$
$C_7H_4Br_2O_2$	$C_7H_4Br_2O_3$
$C_7H_4Br_3O_2$	$C_7H_3B_3O_3$.

If we further consider that the second constituent of diazo-amidobenzoic acid is likewise acted upon by bromine, the number of substances capable of being produced by this reaction is still further increased. I have endeavoured to obtain some of them by recrystallising the mixture from hot water and alcohol.

Bromo-benzoic Acid, $C_7H_5BrO_2$, crystallises in beautiful long plates of a pearly lustre, difficultly soluble in hot water, but readily dissolved by alcohol and ether.

Tribromobenzoic acid, $C_7H_3Br_3O_2$, is obtained in small needle-shaped prismatic crystals, which, in their deportment with solvents, differ but little from the preceding compound. They may be volatilized without decomposition.

Chlorine in every respect resembles bromine in its action upon diazo-amidobenzoic acid. The double acid is decomposed with evolution of nitrogen and formation of chlorinated derivatives.

The action of iodine upon diazo-amidobenzoic acid is less energetic than that of bromine; dry iodine-vapour does not attack the acid at all. It is, on the other hand, easily decomposed when suspended in hot water and treated with iodine. The iodine-vapours soon change the original compound into a brown, nearly insoluble, crystalline body, and into a second substance, which is dissolved by the water; a considerable evolution of nitrogen takes place at the same time. The first substance is obtained in a state of purity by dissolving it in very dilute alcohol, digesting with animal charcoal, and once re-crystallising the product from

alcohol and ether. It is a well defined acid, and appears generally in long, narrow, nearly colourless plates, which, by the application of a gentle heat, may be sublimed without decomposition. On rapidly heating them they are decomposed with evolution of iodine-vapour. A combustion made of the pure acid gave numbers leading to the formula of iodoxybenzoic acid $C_7H_5IO_3$.

The second product which remains dissolved in the water is obtained by evaporating the solution and recrystallising the residue from boiling water. It is hydriodate of amidobenzoic acid.

The following simple equation elucidates the formation of these two substances:—

$$C_{14}H_{11}N_3O_4 + I_2 + H_2O = C_7H_5IO_3 + C_7H_7NO_2.HI + N_2.$$

Action of Nitric Acid upon Diazo-amidobenzoic Acid.—Diazo-amidobenzoic acid is immediately destroyed by fuming nitric acid, with evolution of light. In ordinary concentrated nitric acid it dissolves readily with a reddish colour; on heating, however, a violent reaction ensues, the liquid rapidly frothing up whilst quantities of red fumes are evolved. On evaporating the excess of nitric acid on the water-bath, a powerfully acid viscid residue is obtained, which is frequently interspersed with crystals, and is readily taken up by all solvents. It consists chiefly of a new crystallisable acid which may be purified in the following manner. The residue is dissolved in water and the solution treated with an excess of baryta-water, by which a resinous matter is thrown down. After separating the precipitate, the solution is freed from the excess of baryta by passing a stream of carbonic acid, then filtered, and the filtrate is evaporated on the water-bath until a crystalline pellicle appears on the surface. On cooling, a quantity of the barium-salt formed crystallises out in thick yellow needles. By again evaporating the mother-liquor, the remainder of the salt is obtained.

After the salt has been purified by several re-crystallisations, it is dissolved in water and mixed with a quantity of sulphuric acid, just sufficient to precipitate the whole of the baryta. The solution, when evaporated, yields the new acid in rhombic prisms of a yellow colour, which, when re-crystallised from alcohol or ether, are perfectly pure. An analysis of the substance dried at 100° gave numbers corresponding to the formula $C_7H_3N_3O_9$.

I propose for it the name of *trinitrooxybenzoic acid*. It is a bibasic acid, and its constitution may be expressed by the following formula :—

$$C_7H_3(NO_2)_3O_3.$$

It crystallises in well defined rhombic prisms, and is extremely soluble in water as well as in alcohol and ether. The acid, when dry, is nearly white, yet its solution possesses an intense yellow colour, and like picric acid imparts that colour to animal membranes. It has an intensely bitter taste, melts when warmed, and deflagrates at a higher temperature. Sulphide of ammonium reduces it with formation of a new body and separation of sulphur. It combines with bases forming well defined salts, nearly all of which are soluble in water, whilst some are beautifully crystallised. I have only examined a few of them.

Trinitrooxybenzoate of Barium.—$C_7HBa_2(NO_2)_3O_3$ is easily soluble in water; a boiling saturated solution, however, deposits but few crystals on cooling, its solubility in hot and in cold water differing but little. By spontaneous evaporation of the aqueous solution this salt is obtained in thick needle-shaped concentric crystals of an intense yellow colour. They are all but insoluble in alcohol and ether, and extremely explosive. They contain water of crystallisation, part of which they lose on being dried over sulphuric acid.

The *ammonium-salt* is prepared by saturating the acid with aqueous ammonia; it forms yellow prisms, easily soluble in water, but difficultly soluble in alcohol; they resemble picrate of ammonium in many respects.

The *silver-salt*, $C_7HAg_2(NO_2)_3O_3$, appears in the form of yellow globular crystals, easily soluble in water.

Action of Nitrous Acid upon Diazo-amidobenzoic Acid.—The products which are obtained on submitting the double acid to the decomposing influence of nitrous acid differ according to the presence either of alcohol or of water.

Action of Nitrous Acid in the presence of Water.—The double acid when suspended in boiling water and submitted to a current of nitrous acid, is completely decomposed, with evolution of gas; the resulting red liquid on cooling deposits a reddish crystalline substance. Recrystallisation from boiling water, with addition of a little animal charcoal, yields it in beautiful narrow plates of a light yellow colour. This substance is *nitrooxybenzoic acid* $C_7H_5(NO_2)O_3$, already described by Gerland.

Action of Nitrous Acid in presence of Alcohol.—On suspending diazo-amidobenzoic acid in alcohol saturated with nitrous acid, and passing a current of the same gas through the liquid, whilst the whole is kept in ebullition, exactly the same phenomena are observed as those previously enumerated. The double acid is rapidly dissolved, with formation of a deep, brownish-red solution, and simultaneous evolution of nitrogen. On evaporating the alcohol as soon as the double acid has completely disappeared, a reddish-brown residue is obtained, consisting chiefly of a crystallisable volatile acid.

To purify this acid, it is sublimed in a retort, in order to separate it from the accompanying non-volatile resin. By repeating this operation several times, or by recrystallising the sublimed acid from boiling water, it is obtained in white indistinct needles or plates, having the composition of benzoic acid.

If we neglect the formation of the red resin, the formation of the benzoic acid may be illustrated by the following equation :—

$$\underset{}{C_{14}H_{11}N_3O_4} + \underset{\text{Alcohol.}}{2C_2H_6O} + NHO_2 = \underset{\text{Benzoic acid.}}{2C_7H_6O_2} + \underset{\text{Aldehyde.}}{2C_2H_4O} + 2H_2O + 4N.$$

Action of Ammonia upon Diazo-amidobenzoic Acid.

Diazo-amidobenzoic acid dissolved in dilute aqueous ammonia is easily decomposed on boiling, with evolution of nitrogen gas. If the dark, reddish-brown liquid obtained be evaporated on the water-bath, and treated with dilute hydrochloric acid, a reddish-brown amorphous body is precipitated, whilst the mother-liquor contains a second product of decomposition. The red body is purified by dissolving in alcohol, precipitating with water, and desiccating over sulphuric acid. It is a red, amorphous powder, insoluble in water and ether, but easily soluble in alcohol. It possesses the character of an acid, dissolving with facility in alkalies, from which it is reprecipitated by acids. A neutral solution of the acid in ammonia gives brown amorphous precipitates with solutions of metallic salts. I have not determined its composition.*

The mother-liquor containing the second product of decomposition is evaporated, and the chloride of ammonium precipitated by

* Relying upon a single combustion, I had set up for this body the formula $C_{14}H_{10}O_5$. I have since found that it contains nitrogen; and I intend to submit it to investigation at some future time.

dichloride of platinum. The precipitate is filtered off, and the filtrate saturated with sulphuretted hydrogen; the sulphide of platinum is separated; and the solution evaporated on the water bath. The residue consists of amido-benzoic acid *combined* with hydrochloric acid.

Exactly the same decomposition takes place when diazo-amidobenzoic acid is acted upon by a dilute solution of potash.

I have performed the experiment just described in many different ways. Nothing appears more simple than to suppose that diazo-amidobenzoic acid under the influence of alkalies splits up thus:

$$C_{14}H_{11}N_3O_4 + H_2O = C_7H_6O_3 + C_7H_7NO_2 + N_2.$$

There would accordingly exist in diazo-amidobenzoic acid, that is in its pre-existing atomic group, $C_7H_4N_2O_2$, an intermediate body, by means of which it might have been easy to step from the amido-acids to the corresponding oxyacids. However all the experiments I have made with this object have failed, the result being always amidobenzoic acid and the same red amorphous body.

These facts give a sufficiently clear representation of the chemical deportment and the nature of diazo-amidobenzoic acid. I might have considerably increased the number of products of decomposition, as there are many other bodies which induce an alteration of diazo-amidobenzoic acid; but in order not to extend the limits of this investigation too far, I have preferred to abstain from communicating further experiments made in this direction.

Diazo-amidoanisic Acid.

Anisic acid, although not standing in the same homologous series with benzoic acid, yet exhibits a great analogy with it in its whole chemical and physical deportment, an analogy which is sustained throughout nearly all the derivatives of both these substances.

It was to be expected that amidoanisic acid, under the influence of nitrous acid, would be converted into a compound possessing those properties which are so characteristic in diazo-amidobenzoic acid. Experiment has entirely confirmed this supposition. The new compound is obtained by exactly the same method as that

employed for the preparation of diazo-amidobenzoic acid. A current of nitrous acid gas is passed into a cold saturated solution of pure amidoanisic acid, or the latter is treated with an ether of nitrous acid. In both cases, the substance required separates as a yellowish green amorphous powder; it is collected on a filter, and purified by repeatedly washing with alcohol. It deserves here to be particularly noticed, that in order to ensure the success of this experiment, it is above all things necessary to operate at a low temperature, and carefully to avoid an excess of nitrous acid; as otherwise the desired substance is not even always formed, and if formed is re-dissolved with the greatest facility, and converted into another product. The latter phase is at once recognised by the commencement of an evolution of gas, as well as by the appearance of a deep brownish-red colour. It is best not to operate upon large quantities, and the operation succeeds well if the solution of amidoanisic acid is introduced into a number of test-tubes, and these severally submitted to the action of nitrous acid. The separate portions may then be mixed and purified, as before described. The formation of the new substance takes place thus:—

$$\underset{\text{Amido-anisic acid.}}{2C_8H_9NO_3} + NHO_2 = \underset{\text{New acid.}}{C_{16}H_{15}N_3O_6} + 2H_2O.$$

One glance at the mode of formation, and at the few properties already known of this substance, suffices to stamp it as the true analogue of diazo-amidobenzoic acid. I have called it *diazo-amido-ansinic acid*, and consider its rational composition to be expressed by the formula,—

$$\left\{\begin{matrix} C_8H_6N_2O_3 \\ C_8H_7(NH_2)O_3 \end{matrix}\right\}$$

It presents itself in the form of a yellow, or greenish-yellow amorphous powder, and but seldom exhibits traces of crystalline form. It is insoluble in water, as well as in alcohol and ether. Powerful acids dissolve it, though not without decomposition. In aqueous solutions of the alkalies, on the other hand, it dissolves without alteration, if the temperature be kept below the boiling point. Weak acids precipitate from these solutions the original substance as a yellow gelatinous mass. It may be dried at 100°, without danger, and is decomposed only at a considerably higher

temperature. Heated on platinum-foil, it deflagrates slightly, the residue then melting and burning quietly with a smoky flame.

Salts of Diazo-amidoanisic acid.—Diazo-amidoanisic acid is a double acid, which, like its analogue in the benzoic group, always combines with two equivalents of metal. Its salts are partly of great beauty; and whilst possessing but little stability when in aqueous solution, will, when dry, bear a temperature exceeding 160°. Its salts with the alkalies are alone soluble in water, the rest forming, almost without exception, yellow or greenish-yellow precipitates.

The potassium-salt, $C_{16}H_{13}K_2N_3O_6$, is obtained by dissolving the acid in an excess of carbonate of potassium. If the temperature be maintained below 80°, nothing but carbonic acid is evolved; the solution assumes a yellowish-green colour. On cooling, the salt is deposited in golden yellow oval plates; they are collected on a filter, and washed with very dilute alcohol until it runs off nearly colourless. In order to recrystallise this salt, a process which is not always successful, it is dissolved in the least possible quantity of water at about 80°, from which the greater portion separates on cooling. It is scarcely possible to obtain the remainder of the salt by concentrating the mother-liquor, as, on doing so, an evolution of gas soon commences; the colour of the solution also changes from yellowish-green to a deep brownish red, thus indicating the decomposition of the substance. The salt when dried over sulphuric acid, has the composition $C_{16}H_{13}K_2N_3O_6.2H_2O$.

The water of crystallisation is expelled only at about 160°.

The crystals, especially when floating in the solution, exhibit a vivid scintillation, resembling crystallised iodide of lead suspended in water. The salt is easily soluble in warm water; difficultly soluble in a concentrated solution of carbonate of sodium or potassium; insoluble in alcohol and in ether. From a concentrated aqueous solution it is precipitated by alcohol as a light yellow powder. It deflagrates at 180°. Its solution in water has no action on vegetal colours.

Diazo-amidoanisate of sodium, $C_{16}H_{13}Na_2N_3O_6$, is prepared in exactly the same manner as the potassium-salt, which it resembles in all respects. It crystallises in well-defined six-sided plates, of a golden-yellow colour, and is less soluble in water than the potassium compound. When dried over sulphuric acid, it still retains $1\frac{1}{2}$ molecules of water of crystallisation.

Diazo-amidoanisate of ammonium forms readily soluble golden-

yellow plates. The aqueous solution is rapidly decomposed by ebullition.

Magnesium-salt.—Greenish-yellow globular masses of crystals, difficultly soluble in water.

With the alkaline earths and the metals, diazo-amidoanisic acid forms insoluble, or nearly insoluble salts, which separate as yellowish-green gelatinous masses.

Diazo-amidoanisate of Ethyl, $C_{16}H_{13}(C_2H_5)_2N_3O_6$, is obtained by acting upon an alcoholic solution of amidoanisic ether with nitrous acid. If a moderately concentrated solution has been employed, the new ether at once separates in small crystals. By separating the mother-liquor and recrystallising the substance from alcohol it is obtained perfectly pure for analysis.

Diazo-amidoanisate of ethyl is easily soluble in hot alcohol; the greater part of it crystallises out on cooling in the form of long narrow plates of a yellowish-red colour. Ether likewise dissolves it, but it is insoluble in water. It is not volatile without decomposition. When heated on platinum-foil, it fuses and gives off volatile products of decomposition, and finally burns with a smoky flame. The new ether possesses the character of a weak base; it dissolves very sparingly in dilute acids, and is reprecipitated by ammonia. Concentrated acids and alkalies decompose it in the same manner as the free acid.

Diazo-amidoanisate of Methyl, $C_{16}H_{13}(CH_3)_2N_3O_6$, is obtained from amidoanisate of methyl, in exactly the same manner as the ether mentioned before. It forms yellowish-red plates, which in nearly all their properties resemble the preceding compound.

Products of decomposition of Diazo-amidoanisic Acid.

In its deportment with reagents, diazo-amidoanisic acid exhibits the same mutability as the corresponding compound in the benzoic group. The resulting products of decomposition are throughout analogous to those of diazo-amidobenzoic acid. I will here give a short description of a few of them.

Decomposition with Hydriodic Acid.—On heating the new acid with hydriodic acid, *Iodanisic acid,* $C_8H_7IO_3$, and hydriodate of amidoanisic acid are formed, with abundant evolution of nitrogen. The first compound separates as a reddish crystalline mass, whilst the

latter remains dissolved in an excess of hydriodic acid. Iodanisic acid, when perfectly pure, appears in the form of exceedingly small needles, almost insoluble in alcohol, ether, and in water.

Hydriodate of amidoanisic acid, obtained by evaporating the hydriodic mother-liquor, is extremely soluble in water, easily soluble in alcohol. It crystallises in plates or needles, and frequently in star-shaped groups. The transformation of diazo-amidoanisic acid under the influence of hydriodic acid is represented by the following equation :—

$$C_{16}H_{15}N_3O_6 + I_2H_2 = C_8H_7IO_3 + C_8H_7(H_2N)O_3.HI + N_2.$$

It is remarkable that the decomposition of diazo-amidoanisic acid by hydrochloric and hydrobromic acid is totally different from that with hydriodic acid. No traces of chloranisic or bromanisic acids are formed; the resulting products are amidoanisic acid and a brownish-red acid insoluble in water, which I have not yet thoroughly examined.

Exactly the same products arise when a solution of diazo-amidoanisic acid is boiled for some time with an alkali.

Chlorine, bromine, and iodine also act upon diazo-amidoanisic acid; the products which arise I have not yet examined; neither have I followed up the transformations which the acid undergoes under the influence of sulphuric and nitric acids.

Action of Nitrous Acid upon Diazo-amidoanisic Acid in the presence of Alcohol.—When suspended in boiling alcohol and treated with a current of nitrous acid gas, the new acid is rapidly decomposed with evolution of nitrogen. On distilling off the alcohol, a residue is obtained consisting of an acid, which, when re-crystallised, in order to separate it from a resinous body with which it is mixed, appears in the form of small prisms exhibiting all the properties of ordinary anisic acid.

Its formation takes place thus :—

$$C_{16}H_{15}N_3O_6 + NHO_2 + 2C_2H_6O = \underset{\text{Anisic acid.}}{2C_8H_8O_4} + \underset{\text{Aldehyde.}}{2C_2H_4O} + 2H_2O + N_4.$$

The experiments just described will suffice to show the intimate relation which exists between diazo-amidoanisic acid and diazo-amidobenzoic acid. In fact, there are but few bodies to be found which exhibit so great an analogy, both in their physical and

chemical deportment. This analogy is carried to a still higher degree in the following compounds, so that it would be but a repetition of the previous pages to enumerate their properties in detail.

Diazo-amidotoluylic Acid.

The preparation of this compound from amidotoluylic* acid is identical with that of diazo-amidobenzoic acid.

Its formation takes place according to the following equation:—

$$2C_8H_9NO_2 + NHO_2 = C_{16}H_{15}N_3O_4 + 2H_2O.$$

It crystallises in yellow microscopic prisms, which differ from the crystals of diazo-amidobenzoic acid only in their superior size. It is insoluble in water as well as in alcohol and ether; acids dissolve it with decomposition; the alkalis, on the other hand, dissolve it without alteration. When heated on platinum foil, it deflagrates, and then burns with a smoky flame. It is inodorous and tasteless.

I have made only a few qualitative observations on the salts of diazo-amidotoluylic acid.

Diazo-amidotoluylate of potassium forms a crystalline mass easily soluble in water.

The same may be said of the sodium- and the ammonium-salt. The aqueous solution of the latter especially is easily decomposed on ebullition.

Diazo-amidotoluylate of barium, prepared by precipitating the ammonium-salt with chloride of barium, is a yellow precipitate insoluble in water and in alcohol.

Diazo-amidotoluylate of silver is also a precipitate which, on account of its gelatinous nature, can be separated only with difficulty from the mother-liquor.

* The amidotoluylic acid was prepared from Noad's toluylic acid. I still consider this acid, obtained by the oxidation of cymene by nitric acid, as the true homologue of benzoic acid, in spite of the reasons brought forward by Strecker and Möller (Ann. Ch. Ph. cxiii., 67) against this view. For although these chemists, relying on observations of the melting point and the form of crystallisation of the toluylic acid discovered by them, pronounced it to be the true homologue of benzoic acid, yet the deportment of their acid with certain oxidising agents, with which it yields oil of bitter almonds, is equally against this view. The manifold derivatives of Noad's toluylic acid which I have prepared, and which are scarcely to be distinguished from the corresponding derivatives of benzoic acid, will assist in restoring this acid to its original place in the system.

The transformations of diazo-amidotoluylic acid under the influence of reagents have also only been qualitatively investigated; they resemble in every way the phenomena described when treating of diazo-amidobenzoic acid. Nitric acid converts it into a yellow crystallisable acid, easily soluble in water and in alcohol, and which is, in all probability, homologous with trinitro oxybenzoic acid. Nitrous acid converts the new acid, when suspended in water, into derivatives of oxytoluylic acid, whilst when suspended in alcohol, it yields an acid which is, no doubt, identical with toluylic acid.

Hydrochloric acid gives rise to the formation of *chlorotoluylic acid,* and hydrochlorate of amidotoluylic acid with simultaneous evolution of nitrogen. Hydrobromic and hydriodic acids give rise to perfectly analogous decompositions. The iodotoluylic acid thus obtained crystallises in delicate white plates or needles, with difficultly soluble in water, easily soluble in alcohol and ether. It greatly resembles iodobenzoic acid. Its formula is $C_7H_7IO_2$.

Diazo-amidocuminic Acid.

$$\left\{\begin{matrix} C_{10}H_{10}N_2O_2 \\ C_{10}H_{11}(H_2N)O_2. \end{matrix}\right\}$$

This acid, of all those just described, is the most difficult to obtain. Its preparation succeeds best in a test-tube surrounded with ice and containing an alcoholic solution of amidocuminic acid, into which a current of nitrous acid is passed, great care being taken to avoid an excess of gas. It is best to stop the current as soon as the solution begins to become turbid from separation of crystals. On allowing the liquid to stand for a short time, the whole of the new substance formed is deposited. It is collected on a filter and purified by washing with cold alcohol.

Diazo-amidocuminic acid crystallises in yellow microscopic prisms or plates, nearly insoluble in cold alcohol, quite insoluble in water. It is the most unstable of all the analogous compounds just described, and is decomposed, with evolution of nitrogen, on merely boiling with alcohol. It exhibits, however, all the characteristic reactions of the double acids previously described.

Diazo-amidocuminate of barium is a yellowish-white amorphous powder.

Diazo-amidocuminate of silver falls as a yellow amorphous

mass on treating an ammoniacal solution of the acid with nitrate of silver.

Appendix.

When describing the preparation of the different double acids, the necessity has always been pointed out of maintaining a low temperature and avoiding an excess of nitrous acid.

The formation of these diazo-amido acids does not take place at all if a large excess of nitrous acid is brought in contact with a hot alcoholic solution of the amido acids. In this case a perfectly different reaction ensues; the atomic group NH_2, which is supposed to exist in the amido-acids, is simply replaced by one atom of hydrogen. The other products are water, aldehyde, and nitrogen, as shown in the following equation: –

$$C_8H_7(NH_2)O_3 + NHO_2 + C_2H_6O = C_8H_8O_3 + C_2H_4O + 2H_2O + N_2.$$

This decomposition succeeds best in the following manner:—Alcohol, previously saturated with nitrous acid, is heated to ebullition, and the solution of the amido-acid then added, whilst a continuous stream of nitrous acid gas is passed through the mixture.

The liquid generally assumes a brownish-red colour, whilst a vigorous evolution of nitrogen takes place and continues until every trace of amido-acid is decomposed. As soon as this point is reached, the excess of alcohol is distilled off and the residualy acid, which is generally of a reddish colour, is purified by recrystallisation and sublimation.

Each of the amido-acids, which I have examined up to the present moment, may in this manner be converted into an acid identical with that from which the amido-acid may be supposed to have originated by nitration and subsequent reduction.

This following formulæ will illustrate this transformation:—

$C_8H_8O_3$	$C_8H_7(NO_2)O_3$	$C_8H_7(NH_2)O_3$	$C_8H_8O_3$.
Anisic acid.	Nitranisic acid.	Amidoanisic acid.	Anisic acid.
$C_7H_6O_2$	$C_7H_5(NO_2)O_2$	$C_7H_5(NH_2)O_2$	$C_7H_6O_2$.
Benzoic acid.	Nitrobenzoic acid.	Amidobenzoic acid.	Benzoic acid.
$C_6H_4(NO_2)_2O$	$C_6H_3(NO_2)_3O$	$C_6H_3(NO_2)_2(NH_2)O$	$C_6H_4(NO_2)_2O$*
Dinitrophenylic acid.	Trinitrophenylic acid.	Amidodinitrophenylic acid.	Dinitrophenylic. acid.

* See page 270 of this journal.

XLVII.—*On Nitro-Compounds* (Part II). *With Remarks on Isomerism.*

By Edmund J. Mills, D.Sc., F.C.S.

The experiments recorded in the preceding part* resulted in a classification of nitro-compounds according to their products of reduction, and in a contribution to the solution of the problem of the isomerism of the two nitranilines. The present part is chiefly devoted to the consideration of the two nitrobenzoic acids, and some general remarks are appended on the subject of isomerism itself.

(1) *Nitrobenzoic Acid.*

By the name *alpha*-nitrobenzoic acid I designate the solid product of the action of absolute nitric on ordinary benzoic acid. This is at present the only trustworthy process for obtaining it. The preparation is somewhat tedious, thorough nitration being effected only after eighteen hours boiling of the mixture, and nitric acid being repeatedly added to replace that which is lost by evaporation. After cooling and addition of water, nitrobenzoic acid separates out; it may be purified by continued washing with the precipitant.

The term *beta*-nitrobenzoic acid may be applied to that variety which was obtained by treating crude toluol with nitric acid, by Fischer† (who named it "paranitrobenzoic acid") and Wilbrand and Beilstein‡ (who distinguished it as "nitrodracylic acid"), and in all probability much earlier by Abel.§

β-Nitrobenzoic acid has been examined with considerable detail by several chemists, who have formed from it a large number of derivatives similar to, but not identical with, those derived from the sister compound. My object was to ascertain, if possible, the source of this difference. In preparing the second acid, Wilbrand and Beilstein's method was followed precisely, with the exception of the final crystallisation from alcohol, which was found unnecessary. The fact that dinitrotoluol accompanies this body in large quantity is a very remarkable circumstance. The mem-

* Journ. Chem. Soc. [2] ii. 153.
† Ann. Ch. Pharm. cxxvii, 137.
‡ Ann. Ch. Pharm. cxxviii, 257.
§ Ann. Ch. Pharm. lxiii, 313.

bers of the aromatic marsh-gas series, in fact, cannot be advanced to higher stages of nitration than the first without inducing a complicated reaction.

β-Nitrobenzoic acid differs in a most marked manner from the α-modification. The latter is said to dissolve in 400 parts of water* at 10° C.; the former, according to two determinations of my own, in 2,630 parts at 14°. The powder of the less soluble acid is highly electric. The formation of this substance may be approximately expressed by the following equation—

$$6C_7H_8 + 17HNO_3 = 5C_7H_6(NO_2)_2 + \beta C_7H_5(NO_2)O_2 + 15H_2O + 3N_2O_4,$$

which was arrived at by weighing the first two of the specified products, correction being made for the solubility of the latter in the necessary washings.

	Found.		Theory.	
Dinitrotoluol	23·8821 grm.	84·84	5 mol.	84·49
β-Nitrobenzoic acid	4·2670 „	15·15	1 mol.	15·51
	28·1491	100·00		100·00

Combustions and determinations of fusion-point were made both of the two nitrobenzoic acids and the dinitrotoluol, the results yielding very closely the well established numbers of recent observers.

The action of hydriodic acid on the two nitranilines, having borne fruit in some addition to our knowledge of the more intimate nature of those bases, very naturally suggested its extension to the two nitrobenzoic acids, which are immediately related to them. Experiment showed that boiling hydriodic acid of moderate strength produces the corresponding amidobenzoic hydriodates, with liberation of iodine. These salts may be obtained in tolerable purity by evaporating the liquid containing the products of the reaction to dryness, heating the residue to 100° as long as iodine continues to escape, dissolving in water, filtering, and crystallising. A small quantity of a brown substance removed in this process is probably due to the oxidising influence of free iodine.

* I find the acid to dissolve in 352·5 parts of water at 13° C. Higher numbers given by other authors probably refer to a substance obtained with the aid of sulphuric acid, and having a higher fusion-point than normal nitrobenzoic acid (128°).

The *α-hydriodate* dissolves easily in cold ether, alcohol, or hot water, crystallising readily from these solvents. It is a comparatively stable body.

The *β-hydriodate* dissolves less readily, and is soon coloured by exposure to air, especially if the temperature be raised.

Neither of these bodies produces a coloured reaction with argentic nitrate. The following iodine determinations were made:—

(α) 0·5740 grm. substance, dried at 100°, gave 0·5145 grm. argentic iodide.

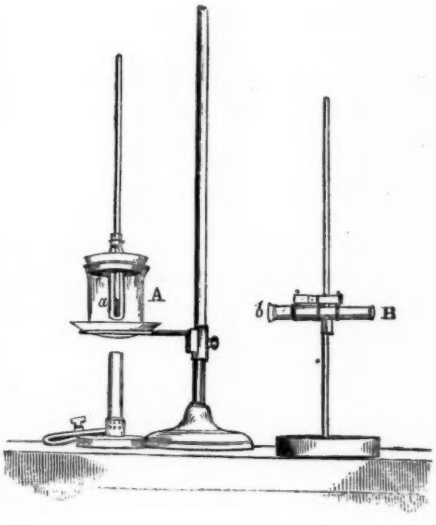
(β) 0·4823 grm. substance, dried at 100°, gave 0·4218 grm. argentic iodide.

	Found.		Theory.
	α.	*β*.	$C_7H_5(H_2N)O_2.HI$.
Iodine	48·44	47·27	47·93

Hence the nitrobenzoic acids belong to the class of "amidogens."

In order to institute a comparison between the temperatures of attack of these substances by hydriodic acid, the same method was employed to which I have already alluded in Part I of these researches. I may be permitted to add here a brief description of the apparatus, which the accompanying figure will help to explain.

A beaker A, more than two-thirds filled with oil of vitriol, is adjusted on a ring-stand in the ordinary manner; its edge supports a thick cork, through the centre of which a hole is bored to admit the tube *a*, in which the reaction is to be performed. This tube contains a smaller one (the "weighing-tube," in which the given substance is weighed), not shown in the figure, which is kept vertical by small beaks, or outward processes, from its edge. An



inclined position would interfere with the result. The tube *a* is furnished at its orifice with a cork having two apertures—one central, to admit a thermometer, and one lateral, to permit the escape of air and vapours. The thermometer is always brought to the same position previous to an experiment by reference to the stem of the ring-stand and any other convenient line, preferably vertical, in the vicinity. The tube B is placed at a suitable distance for observing the gradual obscuration, due to the free iodine, of the band of light occupying the proximate part of the cylindrical bulb of the thermometer. It is merely furnished, at *b*, with an upright glass thread to aid the eye in returning to the same position, and, on its upper part, with a spirit level. It admits of motion both vertically and horizontally. Both it and the ring-stand should be left unmoved throughout a series of observations. The operator's back is towards the light, and the experiments must be performed in the shadow of a partially opaque screen, to avoid the direct illumination of the beaker A. The bath of oil of vitriol in A has its surface on a level with that of the liquid in *a*. It should be heated uniformly, and with tolerable rapidity. The "attack-point" is the temperature at which the cylindrical portion of the bulb of the thermometer ceases to be visible.

The results thus procured show a remarkable difference between the nitrobenzoic acids—a difference greater even than that which obtains in like manner between the two nitranilines. The numbers are given in a table accompanying the present paper,* and curves are drawn to facilitate an immediate comparison. The necessary details of the apparatus, for which alone these results are here taken to hold good, are as follow:

Oil of vitriol in the bath	250 c.c.
Internal diameter of *a*	13·62 m.m.
Diameter of thermometer	3·80 ,,
Thickness of weighing tube	0·37 ,,
Hence width of obscured annulus ..	4·54 ,,
Volume of hydriodic acid employed ..	5·00 c.c.
Weight of substance taken	0·20 grm.
Rate of heating	1° in 11 seconds.

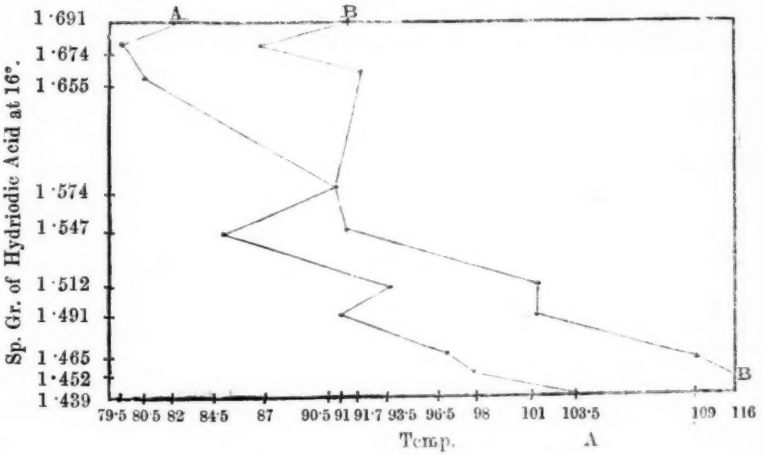
(2) *Action of Nitric on Benzoic Acid.*

The experiments of Wilbrand and Beilstein, already alluded to have shown that β-nitrobenzoic acid may be successively

* See opposite page.

transformed by known reactions into β-amidobenzoic, β-azo-amidobenzoic and benzoic acid. It was left an open question by those chemists whether the substance last produced was absolutely identical with ordinary benzoic acid, or different from it. The resemblance is, indeed, most remarkable. It has been already pointed out that in fusion-point, solubility in water and form of the calcium-salt*, there is no practical distinction between these bodies. I may add that their ethylic ethers are precisely alike in odour, a point on which frequent stress is laid in distinguishing isomeric substances. In order to decide this point, if possible, I submitted both ordinary benzoic acid and that derived from β-nitro-benzoic to the action of nitric acid, in the manner already described at the commencement of this paper. The liquid finally obtained was not precipitated with water, but evaporated to dryness at 100°. When the free nitric acid had completely volatilised, and the product had been allowed to cool, a gummy mass presented itself, in which crystals speedily made their appearance. The whole was transferred to a quantity of filter-paper, and heated to 100° for a few hours. White crystals were then found on the upper surface of the paper, while a very easily fusible substance had soaked down to its interior. The crystals are readily purified by means of alcohol, in which, as well as in ether, they rapidly dissolve in the cold; in boiling water they dissolve but sparingly;

CURVES ILLUSTRATING THE ATTACK OF ALPHA-NITROBENZOIC AND BETA-NITROBENZOIC ACID.



* Wilbrand and Beilstein, loc. cit.

in water at 15° scarcely at all. With caustic potash there is first a violet, and then a red coloration; but not solution, unless the liquid has been weak. These remarks, with the exception of the reaction just mentioned (which belongs to the derivative from the source β), apply equally to both bodies.

The fusion-point of the nitro-compound (from ? β-benzoic acid) was 201°·9 (cor.); its composition that of *di*nitrobenzoic acid.

0·2655 grm. substance, dried at 100°, gave 0·3802 grm. carbonic dioxide, and 0·0569 grm. water.

	Found.	Theory.
Carbon	39·05	39·62
Hydrogen	2·38	1·89

The readily fusible body occurring with this is extracted from the paper by ether, the solution filtered, evaporated to dryness, and the residue heated to 100° till constant. Thus prepared it probably contains a small quantity of the preceding compound, with which it agrees closely in its reactions; it is, however, more soluble in alcohol or ether. It melts at 88° (cor.), and scarcely solidifies on cooling.

0·37635 grm. substance, dried over oil of vitriol, gave 0·6044 grm. carbonic dioxide, and 0·1035 grm. water.

		Theory.	
	Found.	$C_7H_4(NO_2)_2O_2$	$C_7H_5(NO_2)O_2$
Carbon	43·79	39.62	50·30
Hydrogen	3·06	1·89	2·99

This product, therefore, is intermediate in composition between mono-nitrobenzoic and dinitrobenzoic acid, but decidedly approaches the latter.

The white crystals obtained from common benzoic acid, as mentioned above, melt at 137°·5 (cor.); after re-crystallisation from dilute nitric acid, washing, and drying, the fusion-point is 136°·3 (cor.)—a very slight alteration. They dissolve in 422·2 parts of water at 13°; and constitute, I believe, a definite compound.

0·3391 grm. substance, dried at 100°, gave 0·6225 grm. carbonic dioxide, and 0·1006 grm. water.

	Found.	Theory. $C_7H_5(NO_2)O_2$
Carbon	50·07	50·30
Hydrogen	3·29	2·99

Hence these crystals have the composition of *mono*nitrobenzoic acid, but are not physically identical with it. I have not yet examined the more fusible body which accompanies them, and which appears to have hitherto escaped the notice of chemists.

The following experiments have a very important bearing on those just described :—

(3) *Simultaneous Action of Sulphuric and Nitric Acid on Ordinary Benzoic Acid.*

When benzoic acid is heated to 100° in a closed vessel with sulphuric and nitric acids, and the liquid cooled and mixed with water, a white crystalline precipitate falls, the yellow mother-liquid retaining in solution at least one other product. The nature of the result varies according to the time of digestion, and the quantity and strength of the mixed acids.

(1) *The precipitate.*—It is immaterial whether benzoic or α-nitrobenzoic acid has been used as the starting point. In either case, the product continues for some time to exhibit the composition of mononitrobenzoic acid, with an increased fusion-point and (it cannot be doubted) a decreased solubility. This fusion-point is always higher than 128°, provided the first stage of nitration has been reached.

One precipitate of this kind coincided remarkably with the white crystals last described in the preceding section. The substance fused at 136°·4 (cor.).

0·3225 grm. substance, dried at 100°, gave 0·5956 grm. carbonic dioxide and 0·0933 grm. water.

	Found.	Theory. $C_7H_5(NO_2)O_2$
Carbon	50·37	50·30
Hydrogen	3·21	2·99

If the action be continued beyond six hours, especially if absolute nitric acid be used, the nitration advances a stage further, and dinitrobenzoic acid is obtained. This appears to be a definite product, and has already been studied by Voit.* Neither his results nor my own, however, agree with those of Cahours; the time of preparation is not short, nor is the fusion-point of the

* Ann. Ch. Pharm. xcix, 100.

acid a low one. On the contrary, it melts at 206°·7 (cor.) I may add also the following numbers :—

0·4196 grm. substance, dried at 100°, gave 0·6190 carbonic dioxide, and 0·0821 grm. water.

	Found.	Theory.
Carbon	40·23	39·62
Hydrogen	2·18	1·89

(2) *The mother-liquid.*—This is filtered from the precipitate, and the sulphuric acid it contains exactly removed by means of barytic hydrate, nitrate, or carbonate. The residual solution is evaporated to dryness, ultimately at 100°. The cooled crystalline mass, which is invariably coloured, yields a perfectly colourless product on extraction with carbonic disulphide. This body may be either *mono*nitrobenzoic acid, or a mixture of that compound with small quantities of dinitrobenzoic acid.

The nitrobenzoic acid obtained in this way fused first at 127°·5 (cor.); after cooling to solidification, it melted at 122°·4 (cor.). Another preparation melted at 122°·3 (cor.). It gives a red colouration with caustic potash.

0·3508 grm. substance, dried at 100°, gave 0·6393 grm. carbonic dioxide, and 0·1080 grm. water.

	Found.	Theory.
Carbon	49·70	50·30
Hydrogen	3·42	2·99

As an instance of the mixed result, I may adduce the following numbers :—

0·2812 grm. substance, dried at 100°, gave 0·4921 grm. carbonic dioxide, and 0·825 grm. water.

	Found.
Carbon	47·73
Hydrogen	3·26

(4) *Simultaneous Action of Sulphuric and Nitric Acid on β-Nitrobenzoic Acid.*

When the above named acids are heated together to a temperature of about 115° for several hours, cooled, and cautiously stirred with a moderate quantity of water, a precipitate falls after some

time. The yellow mother-liquid yields a second product on appropriate treatment. If the temperature of digestion be only 100°, only β-nitrobenzoic acid (with *unchanged* fusion-point) separates on the addition of water.

(1) *The precipitate.*—This has the composition of dinitrobenzoic acid. It dissolves very readily in cold alcohol or ether, and to a considerable extent in hot water. The solution is acid to litmus. With caustic potash it gives a beautiful red colouration. The fusion-point of one preparation was 161°·9 (cor.); after keeping several months, during which it was once heated on the water-bath for a few hours, the fusion-point was found to be 184°·3 (cor.) Another preparation gave the number 166°·5 (cor.).

0·2870 grm. substance, dried at 100°, gave 0·4207 grm. carbonic dioxide, and 0·0618 grm. water.

	Found.	Theory.
Carbon	39·98	39·62
Hydrogen	2·39	1·89

(2) *The mother-liquid.*—This was treated precisely as that mentioned in the preceding section. The product, however, having been found to be impure from calcium-salt, was mixed with a little water and primary potassic oxalate, dried, and extracted with ether. The latter solvent, on evaporation, left the body in a pure state, and almost free from colour. The substance melts at 153°·1 (cor.) to a clear liquid; dissolves with remarkable ease in cold alcohol or ether, but only slightly in water, and gives, with potash or ammonia, a beautiful deep red colouration. Rapidly heated alone, it explodes. After fusion it solidifies with extreme reluctance.

0·2920 grm. substance, dried over oil of vitriol, gave 0·4256 grm. carbonic dioxide, and 0·0697 water.

	Found.	Theory. $C_7H_5(NO_2)_2O_2$
Carbon	39·75	39·62
Hydrogen	2·65	1·89

This appears to be the only product remaining in the mother-liquid. Under the circumstances in which I examined it, it probably contained a small amount of the "*precipitate.*"

(5). *General Observations.*

The remarkable difference between the temperatures at which α-nitrobenzoic and β-nitrobenzoic acid are attacked by hydriodic acid points clearly to a difference between the nitryl radicals they contain. This, it will be remembered, was the conclusion arrived at in the case of the two nitranilines, and it may doubtless be extended to many other isomeric nitro-compounds. Whether the nitryl of α-nitrobenzoic acid is, or is not, identical with that of α-nitraniline, is still an open question.

The experiments described in sections (2), (3), and (4) throw considerable light on the point they were intended to decide. It appears from (2)—though, from equal weights of the bodies not having been taken, the results are not absolutely precise—that benzoic acid prepared from gum benzoin is nitrated only with difficulty, whereas that obtained from β-nitrobenzoic acid is nitrated with remarkable ease. Under the circumstances mentioned, a mono-nitrocompound is obtained from the former, a di-nitrocompound from the latter. Now, if the resistance to nitration which ordinary benzoic acid manifests could be sharply overcome, it is clear that we ought to obtain β-nitrobenzoic acids from it. This condition is satisfied by the employment of a mixture of sulphuric and absolute nitric acid; a substance is produced having the composition of *di*-nitrobenzoic acid, and melting at 206°·7. But benzoic acid derived from β nitrobenzoic acid yields, to nitric acid alone, di-nitrobenzoic acid, melting at 201°·9. This is as close an approximation as can be fairly expected. A further proof of the strong resistance which common benzoic acid presents to nitration is found in the contents of the mother-liquids obtained after digesting with sulphuric and nitric acid, and precipitating with water. That from α-nitrobenzoic acid contains altered α-nitrobenzoic acid; that from β-nitrobenzoic acid contains di-nitrobenzoic acid. On the whole, therefore, I consider that there are two species of benzoic acid. Gregory*, long since, observed the occurrence of two potassic benzoates. I intend to examine these interesting bodies still further, persuaded that they are the true sources of all the phenylic isomers.

* Ann. Ch. Pharm. lxxxvii, 125.

(6). *Remarks on Isomerism.*

The great problem of isomerism, still pressing for solution, has hitherto been treated almost solely in accordance with atomic views. The statical theorists who have adopted these, and who suppose all bodies constituted of atoms fixed in space, hold that isomeric substances are produced by a variation of the *position* of some radical or radicals in the same molecule. The attempts to express this in formulæ, and the invention of a corresponding phraseology, are matters almost too familiar to require special notice. On the other hand, the principle of atomic motion—so largely accepted in physics, so little in chemistry—does not seem to have ever been considered available for speculations in this direction. There have been, however, partial indications of the attainment of a theory having no reference to corpuscular notions. Thus Graham* long since enunciated a peculiar doctrine of chemical action, and bestowed the names "zincous" and "chlorous" on the two opposite functions of one and the same element at the instant of disturbance. Brodie,† also, claimed for substances, at the moment of chemical change, a two-fold aspect or "polar" antithesis. Kekulé‡ and others pointed out that, in certain bodies containing replaceable hydrogen, one-half of this exhibits a different property from that shown by the other half; and they employed the terms "alcoholic" and "saline" to express the difference. Now these distinctions in *function*, considered as belonging to certain relative weights of known radicals, have no necessary connection with the doctrine of atoms, though frequently associated with it in ordinary scientific language.

Let us consider a special case of the phenomenon we are discussing. α-Nitrobenzoic acid is produced by the action of nitric upon benzoic acid from gum benzoin; β-nitrobenzoic acid results from the more complicated reaction between nitric acid and toluol, where oxidation as well as nitration takes place. Omitting, for the present, the oxidation observed in preparing the latter isomer, it is obvious that the difference in character whereby we distinguish two kinds of nitryl is conferred during the formation of the substances containing them. The nitryl of the nitric acid is of

* Elements (1842), p. 204. † Phil. Trans. 1850, p. 762.
‡ Lehrbuch, vol. i. p. 130.

one nature; and this nature becomes altered in one or both cases of its transference. If, therefore, we would account for the alteration, we must do so by exploring further the reaction itself: in other words, it is a question of *force*.

That the functional change in nitryl does not depend wholly, by any means, on the composition of the residues with which it is associated, is clear from what we know of the nitranilines and nitrobenzoic acids. That it does not arise from what is termed the "satureability" of these residues is equally obvious. That nitryl influences and is influenced by the nature of what is combined with it is no doubt true to a certain extent; but if the properties of the nitranilines be compared in detail with those of the nitrobenzoic acids, it will become evident that the change alluded to has a logical claim to be considered a distinct phenomenon.

The numerous and remarkable oppositions furnished by isomerism, whether exhibited with respect to solubility, polarisation, fusion-point, basicity or the like, appear to present us only with the following principle of co-ordination,—that we may induce a *permanent* change in the properties of radicals by virtue of certain reactions. The formation of isomeric bodies, indeed, probably depends on precisely the same laws as that of bodies having differences of composition. The substitution of a radical with certain functions, for one with certain other functions but the same composition, differs only in this last respect from the exchange of a radical for one completely distinct; and, without reference to isomerism, it is easy to see that mere composition has a very subordinate bearing on the properties of a substance.

When we reflect that, of the radicals R, r, (having the same composition) we may have $n\,R$ and $m\,r$ simultaneously in a compound, where $n + m$ is a constant quantity, but where n and m may vary, the most complicated cases have a basis of classification. Thus, if the somewhat formidable array of the turpentines owe its number to the opposite natures which hydrogen is undoubtedly capable of assuming,* we should have here

$$n + m = 16;$$

and we might, of course, anticipate more isomers in this group than we are at present acquainted with. Again, with regard to

* For an instance of this see especially Hofmann on Hydrobenzol, Proc. Roy. Soc. xii, 578.

the hydric tartrates, of which there are three well-established species. If we conceive their isomerism to be also due to the functional difference of hydrogen, and that here

$$n + m = 2,$$

we at once account for their number and can deduce, from the small percentage value of the hydrogen concerned, that whatever difference there is must be very small. These, however, are merely hypotheses on two special cases; but I may remark with respect to the latter, that there is no evidence whatever to justify the common statement, that "inactive" hydric tartrate is a compound of the two "active" species, if it be meant that the last two have respectively half the molecular weight of the first.

The general formula of an isomeric group may be written as follows:—

$$(a\mathrm{A},b\mathrm{a}) + (c\mathrm{B},d\mathrm{b}) + (e\mathrm{C},f\mathrm{c}) + (g\mathrm{D},h\mathrm{d}) + \text{etc.}$$

—A, a, &c., being the two opposite forms respectively of the ultimate component radicals; the italics representing their number, and being constant in sum for each of them.

The real problem of isomerism appears to be as follows:—*Under what conditions of action does chemical force induce a permanent alteration in one or more functions of radicals?* This I conceive to be the problem of every-day chemistry itself, which is occupied for the most part with the production of permanently different bodies.

XLVIII.—*On the Synthesis of Tribasic Acids.*

By Maxwell Simpson, M.D., F.R.S.

In a paper which appeared some time ago in the "Transactions of the Royal Society,"* I showed that the cyanides of the diatomic radicals (at least those which form glycols) when treated with potash, yield bibasic acids which contain respectively four equivalents of carbon more than the parent radicals. Analogy would

* Philosophical Transactions for 1861, p. 61.

lead us to infer that the cyanides of the triatomic radicals would suffer a corresponding decomposition when treated with the same reagent, and yield tribasic acids, containing respectively six equivalents of carbon more than the original radicals. Thus, as we obtain in this way from the cyanide of ethylene (to take a particular case) a bibasic acid of the composition $C_8H_6O_8$ (succinic acid), so from the tercyanide of allyl ($C_6H_5Cy_3$), if the analogy holds good, we ought to get a tribasic acid, having the composition $C_{12}H_8O_{12}$:—

$$C_4H_4Cy_2 + 2\left(\begin{matrix}K\\H\end{matrix}\right\}O_2\Big) + 4HO = \left.\begin{matrix}C_8H_4O_4''\\K_2\end{matrix}\right\} O_4 + 2NH_3$$

$$C_6H_5Cy_3 + 3\left(\begin{matrix}K\\H\end{matrix}\right\}O_2\Big) + 6HO = \left.\begin{matrix}C_{12}H_5O_6'''\\K_3\end{matrix}\right\} O_6 + 3NH_3$$

The following experiments were performed with the view of testing the correctness of the above inference:—

The first step towards the solution of this problem is, of course, the preparation of the hitherto unknown body tercyanide of allyl. This body I succeeded in obtaining by exposing to the temperature of a water-bath for about 20 hours, a mixture of 1 equivalent of terbromide of allyl, 3 equivalents of pure cyanide of potassium, and a quantity of alcohol equal to three times the weight of the cyanide, contained in a large glass balloon with a reversed Liebig's condenser attached to it. At the expiration of this time I found that all the cyanide of potassium had been converted into bromide, and that the alcohol, which now contained impure tercyanide of allyl in solution, no longer gave a precipitate with water. The reaction which takes place is expressed by the following equation:—

$$C_6H_5Br_3 + 3KCy = C_6H_5Cy_3 + 3KBr.$$

As soon as the alcohol became cold, it was separated from the bromide of potassium by filtration, and distilled. The residue thus obtained was then digested with cold water and filtered, by which means it was disembarrassed of a large quantity of tarry matter, which remained on the filter.

Having in this way prepared the tercyanide of allyl, the next step is to submit it to the action of caustic potash. Accordingly the filtrate was treated with a strong solution of that alkali, and

exposed to heat so long as ammonia continued to be evolved. The product, which now contained an organic acid combined with the potash, was evaporated considerably, and treated cautiously in a capacious basin, with nitric acid in excess. This liberates the organic acid, and at the same time partially destroys the impurities with which it is contaminated. The excess of nitric acid was then removed by evaporation, at as low a temperature as possible, and the dry residue treated with strong alcohol, which dissolved the organic acid, but not the nitre which accompanied it. The acid, obtained on filtering and distilling off the alcohol, was finally rendered quite pure by subjecting it, in a glass globe with a long neck, to the action of boiling undiluted nitric acid as long as red fumes continued to be evolved. The residue left after the evaporation of the nitric acid now crystallised readily from water. The crystals, dried at 100° Cent., gave numbers on analysis, which establish the formula $C_{12}H_8O_{12}$, as will be seen from the following table:—

	Theory.		I.	II.	III.
		per cent.			
C_{12} ..	72	40·91	40·63	41·24	41·34
H_8 ..	8	4·54	4·66	4·82	4·47*
O_{12} ..	96	54·55	—	—	—
	176	100·00			

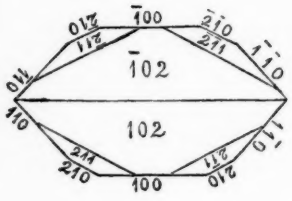
The reaction which generates this body, is explained by the equation given at the commencement of this paper. This acid orms colourless crystals, which are very soluble in water and alcohol, and sparingly soluble in ether. They have an agreeable acid taste. The free acid gives with acetate of lead an abundant precipitate, soluble in strong acetic acid. The neutralised acid forms with perchloride of iron a reddish brown precipitate, from which the acid can be partially removed by solution of ammonia. Neither chloride of barium nor chloride of calcium affects the neutralised acid. An abundant precipitate, however,

* The specimen of acid used in the last two analyses was prepared in a somewhat different manner. The divergence took place at the point in the above process where the mixture of free acid and nitre is digested with alcohol. The acid obtained on evaporating the alcohol, instead of being boiled with nitric acid, was converted into the silver-salt which was afterwards decomposed by sulphuretted hydrogen. It was twice crystallised from water before analysis.

makes its appearance on the addition of alcohol to the mixed solutions. It is a very stable body, not being decomposed by boiling concentrated nitric acid. These reactions resemble those of succinic acid. It is, however, readily distinguished from that acid by its behaviour on exposure to heat. Thus it melts, when exposed to the temperature of about 158° Cent., and when subjected to a higher temperature, suffers decomposition.

The following reaction is, perhaps, characteristic. The solution of the acid, when boiled with freshly precipitated oxide of mercury and filtered, yields on evaporation beautiful white crystals, which have a lustre equal to that of metallic silver.

The following is a description of the crystalline form of this acid, for which I am indebted to Professor Miller, of Cambridge :—*



Prismatic.

Simple forms: 100, 102, 110, 210, 211.

Angles between normals to the faces :—

100	$\bar{1}02$	....	66°	26′
102	$\bar{1}02$	....	47	8
100	$\bar{1}10$	....	46	0
110	$\bar{1}10$	....	88	0
100	210	....	27	22
100	211	....	37	41
110	211	....	32	23
210	211	....	26	59

Cleavage 100, very perfect and easily obtained.

This body has been named by Kekulé† carballylic acid. I cannot, however, accept this name without a slight modification of it, as recent researches have proved that it rightfully belongs to crotonic acid.‡ I propose, therefore, in order to avoid confusion, to call it *tri*-carballylic acid.

I regret to say I have not succeeded in obtaining the tercyanide of allyl in a fit state for analysis. On evaporating a portion of the alcohol, in the midst of which the terbromide of allyle and cyanide of potassium had reacted, a black mass was obtained, which I partially purified by solution in ether. On evaporating

* Professor Miller informs me that these numbers must be looked upon as rough approximations only, the crystals he operated upon not having been quite perfect.

† Lehrbuch der Organischen Chemie. ii, 187. A preliminary notice of this acid has already appeared in the Proceedings of the Royal Society.

‡ Annalen der Chemie und Pharmacie. Band cxxxi, 58.

the ether, a brown liquid was left, which was very soluble in water. This, when gently heated with sodium, gave cyanide of sodium. When treated with potash, it yielded an organic acid and ammoniacal gas. With muriatic acid it gave an organic acid also, no doubt the same, and muriate of ammonia. These three reactions, coupled with the composition of the acid formed in the second, furnish almost conclusive evidence of the generation of tercyanide of allyle by the above process.

I have prepared and analysed several of the salts and ethers of tri-carballylic acid, of which I will now give an account.

Tri-carballylic Ether. $\left.\begin{matrix} C_{12}H_5O_6''' \\ (C_4H_5)_3 \end{matrix}\right\} O_6$.—This body is readily prepared by conducting a stream of dry hydrochloric acid gas into a hot solution of the acid in absolute alcohol; as soon as the reaction is complete, the alcohol is distilled off and the residue washed with a solution of carbonate of soda, and then with pure water. On submitting the oil thus obtained to distillation, I found that almost the entire liquid passed over between 295° and 305° Cent. My analyses of this liquid establish the formula given above, as will be seen from the following table :—

	Theory.		Experiment.	
		per cent.	I.	II.
C_{24} ..	144	55·38	54·59	54·86
H_{20} ..	20	7·69	7·83	7·43*
O_{12} ..	96	36·93		
	260	100·00		

This ether is a colourless liquid, slightly soluble in water, and having an acrid taste. It boils at about 300° Cent. Heated with solid potash, it suffers decomposition, alcohol being formed and the acid regenerated.

Tri-carballylic Amylic Ether. $\left.\begin{matrix} C_{12}H_5O_6''' \\ (C_{10}H_{11})_3 \end{matrix}\right\} O_6$.—Dry muriatic acid gas was conducted into a mixture of one part by weight of tri-carballylic acid and two parts of pure amylic alcohol, maintained at the temperature of boiling water. The acid gradually dissolved during the passage of the gas. As soon

* There was a slight loss of water in this analysis.

as it had entirely disappeared, the stream of gas was interrupted and the liquid was heated in a retort to 220° Cent. It was then partially purified by solution in absolute alcohol and in ether. The numbers I obtained on analysing this liquid, confirm the formula I have given, being as near the required numbers as could be expected from a liquid not purified by distillation.

		Theory.		Experiment.
			per cent.	
C_{42}	..	252	65·28	63·51
H_{38}	..	38	9·84	9·46
O_{12}	..	96	24·88	
		386	100·00	

This ether is a thick, oily liquid, heavier than water and having a very acrid taste. Its boiling point is beyond the range of the mercurial thermometer. I could not observe any symptoms of ebullition at 310° Cent. It bore this high temperature without suffering any apparent decomposition. On heating it in a retort with solid potash, a liquid distilled over, which I recognised to be amylic alcohol, by its boiling point and other properties. The acid of the ether remained in the retort united with the potash.

Glyceri-tricarballylate of Baryta. $\left.\begin{matrix} C_{12}H_5O_6''' \\ C_6H_7O_4' \\ Ba_2 \end{matrix}\right\} O_6$.—A mixture of one part by weight of tricarballylic acid and two parts of pure glycerin was maintained in a sealed tube for several hours at the temperature of 200° Cent. The tube was then opened and a slight excess of a solution of caustic baryta added to its contents. The excess was afterwards precipitated by carbonic acid, and the filtered liquor evaporated to dryness on a water-bath. The residue was then treated with absolute alcohol to remove the uncombined glycerin, and finally dissolved in water and precipitated by alcohol. By these means a light buff-coloured precipitate was obtained, which would not crystallise. Its composition is, I have no doubt, truly expressed by the formula given above, although my analyses do not correspond very well with it.

The following are the numbers I obtained:—

	Theory.		Experiment.	
		per cent.	I.	II.
C_{18} ..	108·0	28·05	28·81	—
H_{12} ..	12·0	3·12	3·82	—
O_{16} ..	128·0	33·25	—	—
Ba_2 ..	153·2	35·58	—	34·01

The acid in the above salt is bibasic; its composition is represented by the formula:—

$$\left.\begin{matrix} C_{12}H_5O_6''' \\ C_6H_7O_4' \\ H_2 \end{matrix}\right\} O_6$$

Its formation is explained by the following equation:—

$$C_{12}H_8O_{12} + C_6H_8O_6 = C_{18}H_{14}O_{16} + 2HO.$$

Soda-salts of Tri-carballylic Acid.—The soda-salts of this acid are very soluble in water and difficult to crystallise. I believe that three salts may be formed containing respectively one, two, and three equivalents of sodium. One equivalent of the acid, I found, required for complete neutralisation, exactly three equivalents of pure, recently-ignited carbonate of soda. I could not obtain this salt in a fit state for analysis. I formed the salt with two equivalents of sodium by adding one equivalent of the acid to two other equivalents which had been previously neutralised, and evaporating the mixture on a water-bath till crystals were formed. These were pressed between folds of blotting-paper and recrystallised. Their composition is very probably represented by the formula:—

$$\left.\begin{matrix} C_{12}H_5O_6''' \\ Na_2 \\ H \end{matrix}\right\} O_6 + 4HO.$$

Dried at 100° Cent., they gave 18·95 per cent. of sodium, instead of 18·7 per cent.

The salt containing one equivalent of sodium would not crystallise.

Tri-carballylate of Lime $\left.\begin{matrix} C_{12}H_5O_6''' \\ Ca_3 \end{matrix}\right\} O_6 + 4HO.$—This salt is readily formed by adding a slight excess of hydrate of lime

to a solution of tri-carballylic acid, and afterwards removing this excess by means of carbonic acid. On evaporating the filtered liquor, a white amorphous powder separates, which is the salt in question. It is very soluble in dilute acids, and sparingly soluble in water. It has the composition represented by the above formula. Dried at 100° Cent., it yielded 23·83 per cent. of calcium, instead of 23·30.

Tri-carballylate of Copper. $\left.\begin{matrix}C_{12}H_5O_6''' \\ Cu_3\end{matrix}\right\}O_6$.—When sulphate of copper is added to a hot solution of tri-carballylate of soda, a beautiful bluish-green powder precipitates, which is the salt in question. It is insoluble in water, but soluble in dilute acids. Its composition accords with the formula I have given. I obtained from the salt dried at 100° Cent., 34·04 per cent. of metallic copper, instead of 35·45.

Tri-carballylate of Lead. $\left.\begin{matrix}C_{12}H_5O_6''' \\ Pb_3\end{matrix}\right\}O_6$.—This salt is obtained by precipitating tri-carballylate of soda with an excess of acetate of lead. It is a perfectly white powder, insoluble in water, but soluble in dilute acids. The formula I have given correctly represents the composition. Dried at 100° Cent., it yielded 63·87 per cent. of metallic lead, instead of 64·23.

Tri-carballylate of Silver. $\left.\begin{matrix}C_{12}H_5O_6''' \\ Ag_3\end{matrix}\right\}O_6$.—When nitrate of silver is added to a solution of tri-carballylic acid, previously neutralised by ammonia, a white precipitate falls, which is the salt in question. This was very carefully washed with distilled water, dried in the water-oven, and analysed. The results I obtained, establish the above formula, as will be seen from the following table:—

	Theory.		Experiment.	
		per cent.	I.	II.
C_{12} ..	72	14·49	14·96	—
H_5 ..	5	1·01	1·20	—
O_{12} ..	96	19·31	—	—
Ag_3 ..	324	65·19		64·05
	497	100·00	—	

This salt is slightly soluble in water, and freely soluble in dilute nitric acid, and in ammonia.

That tri-carballylic acid is tribasic, is, I think, fully established by the manner in which it has been formed, and the composition of the salts and ethers I have just described.

Formulated according to the water and carbonic acid types, it is thus written :—

$$\left.\begin{matrix} C_{12}H_5O_6''' \\ H_3 \end{matrix}\right\}O \qquad 3HO.C_6H_5'''\left\{\begin{matrix} C_2O_2 \\ C_2O_2 \\ C_2O_2 \end{matrix}\right\}O_3$$

The manner of its formation inclines me to prefer the latter formula, although it is more cumbrous. Moreover, it brings out more clearly the relationship that exists between bi- and tribasic acids :—

$$2HO.C_4H_4''\left\{\begin{matrix} C_2O_2 \\ C_2O_2 \end{matrix}\right\}O_2\,; \qquad 3HO.C_6H_5'''\left\{\begin{matrix} C_2O_2 \\ C_2O_2 \\ C_2O_2 \end{matrix}\right\}O_3$$

Succinic acid. (bibasic). Tri-carballylic acid. (tribasic).

This acid is, I believe, at present the sole representative of its class. It will not, however, long remain so, as the process by which it has been obtained will, I have no doubt, prove to be of general application.

Tri-carballylic acid bears the same relation to citric acid that succinic bears to malic acid :

$C_{12}H_8O_{12}$ Tri-carballylic acid.	$C_8H_6O_8$ Succinic acid.
$C^1{}_2H_8O_{14}$ Citric acid.	$C_6H_8O_{10}$ Malic acid.

That this relationship exists not only on paper, but also in the nature of the bodies themselves, we can hardly doubt, when we call to mind that the acid in question has recently been generated from aconitic acid,* one of the products of the decomposition of citric acid by heat, and that acetone, another of these products, is closely allied to the radical from which tri-carballylic acid is derived.

Impressed with these considerations, I have endeavoured to transform this acid into citric acid. The resolution of this problem I have attempted in a great many ways, but hitherto without success. For instance, I have endeavoured to form the bromine compound of tri-carballylic acid, in the hope that it would yield

* Ann. Ch. Pharm. cxxxii. 61.

the desired acid when subjected to the action of hydrated oxide of silver, according to the following equation:—

$$C_{12}H_7Br\,O_{12} + AgO.HO = C_{12}H_8O_{14} + AgBr.$$

My experiments in this direction were, however, cut short by my inability to form the brominated acid. I am at present engaged in endeavouring to solve the inverse problem, namely, the direct transformation of citric into tri-carballylic acid.

XLIX.—*On an Ammoniacal Deposit formed in the process of Drying Blood.*

By John A. R. Newlands, F.C.S.

Some months since, when visiting the premises of Mr. Richard Tons, blood drier, of Bow Common Lane, London, my attention was arrested by the occurrence of a nearly white crystalline deposit adhering to the roof of a shed in which the process of boiling and drying blood was carried on. This deposit was principally found in the further end of the shed where the gases generated in the process found their way into the external atmosphere. It was present in no great quantity, being partly attached to the wooden rafters, but chiefly adhering to the sides of an iron pipe through which steam was occasionally passed.

Some portions of the deposit formed small stalactites, due, probably, to the water produced by a slight escape of steam, having dissolved the crystalline matter, and the resulting solution having evaporated whilst in the act of slowly trickling down. The portion of the deposit immediately adjoining the iron pipe was, as might be expected, mixed up with a layer of peroxide of iron, and the entire mass, just as it came off, on the application of a gentle pressure, gave, on analysis, the following results:—

	Per cent.
Moisture	0·44
Insoluble silicious matter	0·32
Peroxide of iron	1·21
Sulphate of calcium	0·84
Sulphate of ammonium	96·94
Chloride of ammonium	0·07
	99·82

The small quantities of silica and sulphate of calcium were, no doubt, due to the dust from the roof, which was covered with pantiles resting upon wooden beams, some of which appeared to have been whitewashed. The peroxide of iron, as already observed, came from the pipe to which the deposit was attached. The white portion of the crystalline matter, analysed separately, was found to consist of nearly pure sulphate of ammonium.

One word, in conclusion, as to the origin of this deposit. The blood is first raised to the boiling point by the introduction of steam; it is then submitted to the action of a press, and, finally, dried over hot iron plates. During these operations there is a small amount of ammonia evolved, and also traces of sulphuretted hydrogen, and the presence of these gases, in conjunction with the oxygen of the air, and the steam given off, would appear to be quite sufficient to account for the formation of sulphate of ammonium. Whether such formation is preceded by that of sulphuric or sulphurous acids, or of the sulphide or sulphite of ammonium, I do not, for the present, undertake to decide.

P EDINGS

AT THE

MEETI THE CHEMICAL SOCIETY, 1865.

January 19th.

Dr. Miller, F.R.S., Vice-President, in the Chair.

Alfred Noble, Esq., Bristol; J. Carter Bell, Manchester, were elected Fellows.

The following papers were read:—

"On the Artificial Formation of Pyridine:" by Mr. W. H. Perkin.

"Laboratory Memoranda:" by Mr. R. Warington, jun.

"Note on Chemical Nomenclature and Notation:" by Mr. G. C. Foster.

February 2nd.

Professor Williamson, F.R.S., President, in the Chair.

Charles Eastcourt, Esq., Manchester; Arthur Vacher, Esq., 29, Parliament Street; Francis Walker, Esq., Sidney College, Cambridge; John Reid, Esq., Trinity College, Cambridge; Thomas P. Blunt, B.A., Shrewsbury; Robert H. M. Bosanquet, Esq., Oxford; Nathaniel Bradley, Esq., Prescot, Lancashire; Richard Percival, Esq., University, Glasgow; Arthur Smith, Esq., Loughborough-road, Brixton; Thomas Heathcote Windham, Esq., were elected Fellows.

Dr. Hofmann delivered a discourse [illegible]cture Illustrations."

February 16th.

Professor Williamson, F.R.S., Presi[illegible], in the Chair.

The following papers were read:—

"On a New Reaction for the Production of Anhydrides and Ethers:" by John Broughton, B. Sc.

"On the Oxidation of India-Rubber:" by Mr. J. Spiller.

"Note on the Action of Chloropicrin and Chloroform on Acetate of Potash:" by Mr. Henry Bassett.

"On a Dense Brine Spring from Nova Scotia:" by Prof. H[illegible] D.C.L.

March 2nd.

Professor Williamson, F.R.S., President, in the Chair.

The following papers were read:—

"On the Action of Silicate and Carbonate of Soda upon Cotton Fibres:" by F. Crace Calvert, Ph.D., F.R.S.

"On a Crystallised Hydrate of Phenic Acid:" by F. Crace Calvert, Ph.D., F.R.S.

"On some Hydrated Cupric Oxychlorides from Cornwall:" by Prof. A. H. Church, M.A.

March 16th.

Professor Williamson, F.R.S., President, in the Chair.

William Johnson, Ph.D., Newcastle-on-Tyne; George Jones, Esq., 106, Leadenhall-street, were elected Fellows.

The following papers were read:—

"On Vapour-densities:" by Prof. Wanklyn.

"On the Action of Chlorine on Arsenious Acid:" by Professor Bloxam.

University of [illegible]

Anniversary Meeting, March 30th, 1865.

Dr. Williamson, President, in the Chair.

The following report was read by the President:—

Gentlemen,

In accordance with the established practice in our Society, it is my duty to report to you, on the occasion of this Anniversary Meeting, when we come together for the purpose of electing Officers and Council for the ensuing year, the general outline of the progress of the Society during the past year, as well as its present position. This is indeed a most agreeable task, as the steady improvement in the condition of the Society which has been going on for several years past, has continued to manifest itself during the year just expired.

Our members have now increased to 453, besides 38 foreign members, and 6 associates, and the meeting room in which we assemble is being gradually out-grown by the Society.

The Council has taken means to insure a more speedy transmission of our Journal to the foreign members of the Society, and the more frequent publication of the numbers enables us to give earlier publicity than formerly to the papers which are read at our meetings.

There have been thirty-two papers read at our meetings during the year, besides five discussions, including theoretical and practical subjects of great variety, and many of them of great interest.

We have to deplore the death of four of our members, viz.: Dr. R. D. Thomson, Dr. Normandy, Mr. J. B. Neilson, and Dr. Pugh.

Robert Dundas Thomson was the second son of the Rev. James Thomson, D.D., minister of Eccles, Berwickshire, in the manse of which parish he was born on the 21st September, 1810. After spending some time at the grammar school of Dronse, he went to Edinburgh, where he subsequently began the study of medicine. He afterwards continued his studies at Glasgow, where he acquired a fondness for the study of chemistry from the instruction of his uncle, Dr. Thomas Thomson. He graduated at Glasgow in 1831, and after a

voyage to India and China in one of the East India Company's ships, he settled in London as a physician, and lectured on chemistry in the Blenheim-street School of Medicine, whilst engaged in publishing the "Records of Science." From London Dr. Thomson returned for some time to Glasgow, where he assisted his aged uncle in discharging the duties of the Chair of Chemistry. On the death of his uncle, Dr. Thomson was appointed lecturer on chemistry at St. Thomas's Hospital. He also discharged the duties of Medical Officer of Health for the parish of Marylebone, an office for which his chemical, medical, and local knowledge admirably adapted him. There is reason to believe that important improvements in the sanitary state of the parish were brought about through his zealous and enlightened exertions. For about two years his health showed symptoms of decline, and he died on the 13th of August, 1864.

Dr. Thomson was the author of a work entitled "School Chemistry," and also of the "Cyclopædia of Chemistry," and his papers on subjects belonging to kindred sciences are said to have been very valuable. Among the chemical questions which he specially investigated may be mentioned the composition of food and of various waters, the adulterations in drugs, the chemistry of digestion, and of cholera.

He was also an enthusiastic meteorologist, and at the time of his death was President of the Meteorological Society. He was elected a Fellow of the Royal Society of Edinburgh in 1858, and of the Royal Society in 1864. He was also a Fellow of the Chemical Society, and of several other learned bodies.

Dr. Normandy was by birth a Frenchman. He studied chemistry under Leopold Gmelin, and was the author of several books on general and analytical chemistry. He patented and brought into use an apparatus for distilling water, and subsequently purifying it so as to render it fit for drink. The purification is effected by filtration through animal charcoal, with access of air. The introduction of this apparatus has been productive of great benefit to seafarers.

Mr. J. B. Neilson was born at Shettlestown, near Glasgow, in 1792. His active and powerful mind was mainly directed to manufactures, and we owe to him the introduction of one of the most important improvements in the smelting of iron by the use

of the hot blast. The value of the invention is so well known, and so greatly appreciated, that the mere mention of it is sufficient to recall to the mind how great a benefactor Mr. Neilson has been to his own and other countries.

Dr. Evan Pugh, President of the Agricultural College, Pennsylvania, North America, died on the 29th of April, 1864, at the early age of 36.

His father, a farmer in Chester County, Pennsylvania, died when he was very young, leaving his mother and four children in limited circumstances. He was adopted by some relatives, and from his childhood showed marked superiority and intellectual ability; but his friends were unable to afford him any better education than that which was obtainable in the common village school, and at the age of fourteen he was apprenticed to a blacksmith. This was quite opposed to his inclinations, and a severe trial to him; nevertheless it is said that he faithfully performed his duties, while yet devoting every leisure moment to books and study, even often working mathematical problems on the doors and walls of the smith-shop. At the age of nineteen he gained a reluctant consent to abandon this uncongenial occupation, and his next year was spent in a manual-labour seminary in Whitestown, New York. Here he took a high place in the classes and made great advances in knowledge, supporting himself meantime by his trade, and earning enough to make a tour to Niagara and elsewhere.

Having inherited a small farm, he then returned to his native place and established a boarding-school for boys, which was highly successful and remunerative. Two years afterwards he sold his farm, and with this money and the proceeds of his school, was able to carry out his great design of visiting Europe. He spent between three and four years in the Universities of Leipsic, Göttingen, Heidelberg, and Paris, a diligent and successful student of natural and mathematical science. At Göttingen he honourably sustained the examinations for the degree of Doctor of Philosophy.

From the outset his mind had been attracted towards agricultural science, and his studies gradually turned more and more in that direction. Relying upon the interest taken in such subjects by Mr. Lawes and Dr. Gilbert, in December, 1856, whilst at Paris, Dr. Pugh addressed a letter to the latter with a proposition to undertake, in the Rothamsted Laboratory, a new investi-

gation of the question then much discussed, of the assimilation of free nitrogen by plants. Mr. Lawes gladly assented to the proposal, and arrangements were entered into which led to Dr. Pugh's devoting more than two years to the investigation of this and kindred subjects in conjunction with Mr. Lawes and Dr. Gilbert. The results of the inquiry were communicated to the Royal Society, and were published in the Philosophical Transactions, Vol. 151, Part 2, in a paper entitled "On the Sources of the Nitrogen of Vegetation, with special reference to the question whether plants assimilate free or uncombined Nitrogen."

Whilst at the Rothamsted Laboratory, the course of the investigation in which he was engaged, requiring an accurate and easy method for the determination of small quantities of nitric acid, Dr. Pugh perfected a method which has been found very useful by many chemists, and an account of which is published in the Quarterly Journal of the Chemical Society of London, vol. xii, p. 35.

In the autumn of 1859, Dr. Pugh returned to America to assume the Presidency and Professorship of Chemistry of the Agricultural College of Pennsylvania, which had been offered to him. He prosecuted his new duties with great energy and ability, and for rather more than five years laboured unremittingly, in the face of many difficulties, to establish the newly-formed and struggling institution on a secure basis—a result he was just beginning to see realised, when he was suddenly cut off by brain fever after a few days' illness, and within three months of his marriage. The American journals speak of his death as a great loss, not only to the institution over which he presided, but to the cause of scientific education in common with agriculture throughout America.

Besides those mentioned above, Dr. Pugh's published contributions to Science were principally the following:—

"Hämatinsalpetersäure identisch mit Pikraminsäure: *Journal für prakt. Chemie,* lxv, 362.

"Miscellaneous Chemical Analyses: *Inaugural Dissertation,* Göttingen, 1856."

List of Papers read at the Meetings of the Chemical Society, from March 30, 1864, to March 30, 1865:—

1. "On Oxyaniline:" by Dr. Schmidt.

2. "On the Tetrabasic or Ortho-carbonate of Ethyl:" by Henry Bassett.
3. "On the Hexyl Group:" by Prof. Wanklyn and Dr. Erlenmeyer.
4. "On an Alkaloïd obtained from the seeds of *Ricinus communis*:" by R. V. Tuson.
5. "On the action of Hydrobromic acid and of Hydriodic acid upon Polyatomic acids, and on the behaviour of Iodo-substitution-compounds towards Hydriodic acid:" by Professor Kekulé.
6. "On the constitution of Wood-spirit:" by Mr. William Dancer.
7. "On the Chlorophosphide of Nitrogen, and on two new Acids related thereto:" by Dr. J. H. Gladstone and Mr. Holmes.
8. "On a new method of Gas-analysis:" by Drs. Williamson and Russell.
9. "On the Classification of the Elements according to their Atomic Weights:" by Prof. Williamson.
10. "On the identity of Methyl and Hydride of Ethyl:" by Mr. C. Schorlemmer.
11. "On the action of Baryta upon Suberic and Azelaic acids:" by Mr. R. T. Dale.
12. "On the isolation of the Electronegative radicle, Valeryl:" by Prof. Wanklyn.
13. "On the existence of Nitrogen in Steel:" by Messrs. Stuart and Baber.
14. "On the concentration of Nickel in Lead:" by Mr. Baker.
15. "On the blue colour of Forest Marble:" by Prof. Church.
16. "On the effect of ignition on Garnets, &c.:" By Prof. Church.
17. "On the Brine of Salted Meat:" by Dr. Marcet.
18. "On the nature of Compound Ethers:" by Prof. Wanklyn.
19. "Note on the Distribution of Albumen through Muscular Tissues:" by Dr. Marcet.
20. "On the action of Sulph-hydrate of Potassium upon Acetic Ether:" by Prof. Wanklyn.
21. "On the Density of certain Minerals:" by Prof. A. H. Church.
22. "On the action of Ammonia on Sulpho-chloride of Phosphorus:" by Dr. J. H. Gladstone and Mr. J. D. Holmes.

23. "On the Artificial Formation of Pyridine:" by Mr. W. H. Perkin.
24. "Laboratory Memoranda:" By Mr. Robert Warington, jun.
25. "On a new re-action for the production of Anhydrides and Ethers:" by John Broughton, B. Sc.
26. "On the Oxidation of India Rubber:" by Mr. J. Spiller.
27. "Note on the action of Chloropicrin and Chloroform on Acetate of Potash:" by Mr. Henry Bassett.
28. "On a Dense Brine from Saltsprings, Nova Scotia:" by Prof. How, D.C.L.
22. "On the action of Silicate and Carbonate of Soda upon Cotton Fibre:" by Dr. Crace Calvert.
30. "On the Crystallised Hydrate of Phenic Acid:" by Dr. Crace Calvert.
31. "On some Hydrated Cupric Oxychlorides from Cornwall." by Prof. A. H. Church.

List of Discourses delivered at the Meetings of the Chemical Society, between March 30th, 1864, and March 30, 1865.

1. "On the Organic Peroxides theoretically considered:" by Sir Benjamin Brodie.
2. "On the Detection and Discrimination of Organic Bodies by means of their Optical Properties:" by Prof. G. G. Stokes.
3. "On the Philosophy of English Agriculture:" by John Thomas Way, Esq.
4. "On Chemical Nomenclature and Notation:" by Prof. Williamson.
5. "On Lecture Illustrations:" by Dr. Hofmann.

The Treasurer presented the Balance-sheet of the Society duly signed by the Auditors.

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY. Cr.

1864-5.		£	s.	d.	1864-5.		£	s.	d.	£	s.	d.
March 25.	To Balance on hand											
				629	14	11	Journal.	By Editor's Salary to 25th March, 1865	95	0	0	
	„ Yearly Dividend on £900, 3 per cent. Consols, less Income-tax			26	6	6		„ Printing Journal	277	12	0	
	„ Sale of Journals			52	2	0		„ Distributing Journal	38	11	6	
	„ Sundry Receipts from March 25th, 1864, to March 25th, 1865, as below:—							„ Reporting Proceedings	7	7	0	
		£	s.	d.								418 10 6
	Admission Fees	80	0	0	Proceedings of Royal Society.	„ Annual Subscription to Royal Society for their Proceedings sent to the Fellows of the Chemical Society	50	0	0			
	Life Compositions	150	0	0								50 0 0
	Resident Members' Subscriptions previous to 1864	12	0	0	Library.	„ Librarian's Salary to 25th March, 1865	25	0	0			
	Non-resident Members' Subscriptions previous to 1864	7	0	0		„ Books and Magazines	4	5	6			
	Resident Members' Subscriptions for 1864	82	0	0		„ Subscription to Cavendish Society	1	1	0			
	Non-resident Members' Subscriptions for 1864	17	0	0		„ Bookbinding	5	13	10			
	Resident Members' Subscriptions for 1865	362	0	0								36 0 4
	Non-resident Members' Subscriptions for 1865	84	0	0	Collector and Clerk.	„ Collector's Commission	39	14	0			
				794	0	0		„ Clerk	3	0	0	
												42 14 0
							General Printing Stationery, &c.	„ New Receipt and Account Books	4	19	8	
								„ Circulars and Notices	4	10	0	
								„ Postage Envelopes	10	10	5	
								„ Stamps	1	12	7	
								„ Mr. Watts, Stationery and Postage	2	0	0	
												23 12 8
							House Expenses.	„ Royal Society, Share of Tea Expenses	14	19	5	
								„ T. Hux, 1 year's Salary to 25th March, 1865	20	0	0	
								„ „ Petty Expenses as per Book	3	1	7	
								„ „ Gas account	2	4	3	
								„ „ Repairs	2	9	9	
								„ Refreshments, Dr. Hofmann's Lecture	2	0	0	
								„ W. Page, Cleaning	1	1	0	
								„ Gate Porter	2	2	0	
												47 18 0
							Furniture.	„ Power of Attorney				1 1 6
							1864. March 4.	„ Purchase of £100 3 per Cent. Consols				89 17 6
								„ Balance at Messrs Coutts				792 8 11
											£	1502 3 5

ASSETS.	£	s.	d
Balance at Messrs. Coutts	792	8	11
Consols, £1000, 3 per cent, reduced at 89¼ (rate 25th March, 1865)	892	10	0
Subscriptions due:—			
Resident Members 230			
Non-Resident Members 61			
£291 valued at ...	205	0	0
	1889	18	11

Liabilities, None.

All claims against the Society up to 25th March, 1865, have been discharged,

WARREN DE LA RUE.

Examined and found correct, ALFRED SMEE, DANIEL HANBURY, } *Auditors.*

London, March 23rd, 1865.

The following Fellows were elected Officers and Council for the ensuing year:—

President.—W. A. Miller, M.D., F.R.S.

Vice-Presidents who have filled the Office of President.—W. T. Brande, F.R.S., Sir B. C. Brodie, Bart., F.R.S., C. G. B. Daubeny, M.D., F.R.S., Thomas Graham, D.C.L., F.R.S., A. W. Hofmann, LL.D., F.R.S., Lyon Playfair, C.B., F.R.S., A. W. Williamson, Ph.D., F.R.S., Col. P. Yorke, F.R.S.

Vice-Presidents.—Walter Crum, F.R.S., Warren De la Rue, Ph.D., F.R.S., John Stenhouse, LL.D., F.R.S., Robert Warington, F.R.S.

Secretaries.—William Odling, M.B., F.R.S., A. Vernon Harcourt, M.A.

Foreign Secretary.—E. Frankland, Ph.D., F.R.S.

Treasurer.—Theophilus Redwood, Ph.D.

Council.—F. A. Abel, F.R.S., G. B. Buckton, F.R.S., Dugald Campbell, Esq., H. Debus, Ph.D., F.R.S., B. F. Duppa, Esq., G. Cary Foster, Esq., E. A. Hodson, Esq., J. B. Lawes, F.R.S., Hugo Müller, Ph.D., W. J. Russell, Ph.D., Maxwell Simpson, M.B., F.R.S., C. Greville Williams, F.R.S.

It was resolved, that Law IV., relating to the withdrawing and removal of Fellows and Associates be expunged, and the following bye-law be substituted for it:—

"No Fellow shall be at liberty to withdraw from the Society until he shall have paid his arrears, and given to one of the Secretaries a written notice of his intention to resign.

"All Fellows who shall be in arrear of their annual subscription for more than two years, such subscription having been applied for, shall receive notice from the Council that, unless the same be paid within three months, their names are liable to be removed from the list of Fellows."

Any proposition to remove a Fellow or Associate from the Society must be made by the Council. It shall be read at one ordinary meeting of the Society, and at an ordinary meeting next ensuing the proposition shall be balloted for, and if three-fourths of the Fellows voting shall vote for the removal of such Fellow or Associate, he shall be removed from the Society accordingly. The ballot shall not be valid unless twelve or more persons vote.

The thanks of the Society were voted to the President, Officers, Council, and Auditors, for their services during the past year.

April 6th, 1865.

Dr. Miller, F.R.S., President, in the Chair.

Robert Barton, Esq., Bushey Park, Teddington; C. H. Berger, Esq., Lower Clapton; Wm. Chrispin, Esq., Darlington, Durham; Alexander W. Gillmore, Esq., Southfield, Wandsworth; Arthur S. Hobson, Esq., 3, Upper Heathfield Terrace, Turnham Green; Wm. Judd, Esq., Christchurch, Hants; Michael Foster, M.D., Huntingdon; George B. Robertson, Esq., Cathcart Hill, Upper Holloway, were elected Fellows.

The following papers were read:—

"On a new Bromine Derivative of Camphor," by Mr. W. H. Perkin.

"Note on a deposit of Sulphate of Ammonia produced in the process of drying Blood," by Mr. J. A. R. Newlands.

Prof. Wanklyn made a verbal communication on Tindal and Crofts researches on the Ethers.

April 20th, 1865.

Dr. Miller, F.R.S., President, in the Chair.

Arthur C. Bowdler, Esq., Oxford Road, Manchester; W. E. Heathfield, Esq., Princes Square, Finsbury, were elected Fellows.

Prof. Bloxam read some "Laboratory Memoranda."

May 4th, 1865.

M. Holzmann, Ph. D., Marlborough House; Joseph Sugden, jun., Esq., Halifax; J. N. Kirkham, Esq., Gilston Road, West Brompton; were elected Fellows.

The following papers were read:—

"On Phosphide of Magnesium," by Mr. T. P. Blunt.

"On the Periodides of some Organic Bases," by Mr. W. A. Tilden.

May 18th, 1865.

Dr. Miller, F.R.S., President, in the Chair.

Thomas Fairley, Esq., Medical School, Leeds; Edward Swann, Esq., Laboratory, Crewe; Alfred Upwood, Esq., 148, Goswell Street, were elected Fellows.

The following paper was read:—

"On the Specific Refractive Energies of Elements and their Compounds," by Dr. Gladstone.

June 2nd, 1865.

Prof. Williamson, F.R.S., Vice-President, in the Chair.

Dr. Miller delivered a discourse "On some points in the Analyses of Potable Waters."

June 15th, 1865.

Dr. Miller, F.R.S., President, in the Chair.

G. B. Sweeting, Esq., King's Lynn, Norfolk, was elected a Fellow.

The following papers were read:—

"On the Transformation of the Lactic into the Acrylic Series of Acids," by Messrs. Frankland and Duppa.

"On the Action of Nascent Hydrogen on Azodinaphthyldiamine," by Mr. W. H. Perkin.

November 2nd, 1865.

Dr. Miller, F.R.S., President, in the Chair.

James Parkinson, Esq., Royal School of Mines; Frederick Rowe, Esq., Colchester; were elected Fellows.

The following papers were read:—

"On some New Cornish Minerals," by Prof. A. H. Church, M.A.

"On the Caprylic and Œnanthylic Alcohols," by Mr. Ernest Chapman.

"On the Absorption of Vapours by Charcoal," by Mr. John Hunter, M.A.

November 16th, 1865, Extraordinary General Meeting.

Dr. Miller, F.R.S., President, in the Chair.

Resolved, that authority be given to the Council to dispose of the Society's Chemical Specimens in such manner as they may see fit.

Ordinary Meeting.

Wm. Marriott, Esq., Huddersfield; Chas. Amney, Esq., 40, Aldersgate Street, were elected Fellows.

The following paper was read:—

"On Nitro-Compounds," Part II; by Edmund J. Mills, D.Sc.

December 7th, 1865.

Warren De La Rue, F.R.S., Vice President, in the Chair.

John Hunter, Esq., M.A., Fountain Villa, Belfast; Theodore Maxwell, Esq., University College, London; W. J. Barnes, Buckhurst Hill, Essex; W. E. Bickerdike, Esq., Dalton Square, Lancaster; Richard Fitzhugh, Esq., Nottingham; Alfred Gardiner Brown, Esq., Trinity-square, Southwark; W. B. Ritchie, Esq., Belfast, were elected Fellows.

The following papers were read:—

"On Pyrophosphodiamic Acid," by Dr. Gladstone.

"On Phenyl-phosphoric Acid," by Dr. Hugo Müller.

December 21st, 1865.

Dr. Miller, F.R.S., President, in the Chair.

John Percy, M.D., F.R.S., Royal School of Mines; Ernest T. Chapman, Esq.; George V. Portman, Esq.; Charles N. Ellis, Esq., Bow Common-lane; Thomas Ward, Esq., Bolton, Lancashire, were elected Fellows.

The following paper was read:—

"On the Material to be Employed for the Construction of Mural Standards of Length," by Mr. Yates.

Donations to the Library in the year 1865.

"A Dictionary of Chemistry and the Allied Branches of other Sciences;" by Henry Watts: Parts XXIII.—XXXII.;
from Messrs. Longman and Co.

"Modern Chemistry:" by Dr. A. W. Hofmann:
from the Author.

"A Course of Practical Chemistry, adapted to the Use of Medical Students" 2nd Edition: by William Odling:
from the Author.

"Inorganic Chemistry for Science Classes:" by Fearnside Hudson: from the Author.

Fresenius' "Chemical Analysis," 4th Edition: edited by J. Lloyd Bullock and Arthur Vacher:
from Arthur Vacher, Esq.

"Report on the Air of Mines:" by R. Angus Smith:
from the Author.

"The Use of Alcohol as a Test for the Purity of Croton Oil:" by R. Warington: from the Author.

"Lecture on Perfumes, Flower-Farming, and the Methods of Obtaining the Odours of Plants" (delivered before the Royal Agricultural Society): by Septimus Piesse: from the Author.

"Celestial Chemistry and the Physical Constitution of the Stars and Nebulæ;" by Thomas W. Burr: from the Author.

"On Tasmanite:" by A. H. Church.

"Researches on Certain Ethylphosphates:" by A. H. Church:
from the Author.

"The Food of Man in Relation to his Useful Work:" by Lyon Playfair: from the Author.

"Third Report of the Commission appointed to inquire into the best mode of Distributing the Sewage of Towns, and applying it to Beneficial and Profitable Use:" from J. B. Lawes, Esq.

"Essay on the Trees and Shrubs of the Ancients:" by C. B. Daubeny: from the Author.

"Inferences and Suggestions in Cosmical and Geological Philosophy:" by E. N. Brayley: from the Author.

"On Radiation:" by Dr. Tyndall: from the Author.

"The Phenomena of Radiation:" by George Warington: from the Author.

"Address to the Members of the Devonshire Association of Science, Literature, and Art:" delivered at Tiverton, June 28th, 1865: by C. B. Daubeny: from the Author.

"Artificial Lactation:" by C. M. Wetherill: from the Author.

"On the Application of Physiological Tests for certain Organic Poisons, and especially Digitaline:" by C. H. Fogge and Thomas Stevenson: from the Authors.

"On Some Compounds and Derivatives of Glyoxylic Acid: by H. Debus: from the Author.

"A Letter to the Provost of Oriel on University Extension:" by C. B. Daubeny: from the Author.

"Statistics of the Foreign and Domestic Economy of the United States" (1864): communicated by the Secretary of the Treasury: from the Smithsonian Institution.

"Results of Meteorological Observations under the direction of the United States Patent Office, and of the Smithsonian Institution: from 1854 to 1859 inclusive: from the Smithsonian Institution.

"Rapport général sur les Travaux du Conseil d'Hygiène publique et de Salubrité du Département de la Seine" (1849-1858 et 1859-1861): redigé par Adolphe Trebuchet: from the Author.

"Matériaux pour servir à l'histoire des métaux de la Cerite et du Gadolinite:" par M. Delafontaine: from the Author.

"Recherches sur la composition des Molybdates alcalins:" par M. Delafontaine: from the Author.

"Nouveaux Phénomènes des Corps Crystallisés:" par Louis Lavizzari: from the Author.

"Lavori eseguiti nel Laboratorio di Chemica del Real Istituto di Firenze:" da E. Bechi: from the Author.

"I Suffioni boraciferi di Travale:" da E. Bechi:
from the Author.

"Libros del Saber de Astronomia del Rè Don Alfonso de Castilla, compilados, anotados, y comentados por Don Manuel Rico y Sinobras." Tomo iii:
from the Royal Academy of Sciences of Madrid.

"Beschreibendes und theoretisches Handbuch der Chemie:" von William Odling: Deutsche vom Verfasser autorisirte Bearbeitung: von Alphons Oppenheim:
from the Translator.

"Hämatologische Studien:" von Dr. A. Schmidt:
from the Author.

"Lehrbuch der Organischen Chemie:" von Hermann Kolbe: Bd. ii. Lieferungen 1—9: from the Author.

Periodicals:—

"Philosophical Transactions," 1862, part II; 1863, parts I and II; 1864, parts I and II: from the Royal Society.

"List of Officers and Fellows of the Royal Society for the year 1864:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh," vol. XXIII, part 3; and vol. XXII, part 1.

"Proceedings of the same;" Sessions 1863-64, and 1864-65:
from the Society.

"Memoirs of the Royal Astronomical Society," vol. XXIII.
Monthly notices of the same: from the Society.

"Quarterly Journal of the Geological Society," for 1865:
from the Society.

"Quarterly Journal of Science," for 1865: from the Editor.

"Proceedings of the Royal Institution of Great Britain," vol. V.

"List of Members, Officers, and Professors of the same," for 1865: from the Royal Institution.

"The Mining and Smelting Magazine," for 1865:
from the Editor.

"Calendar of the Science and Art Department of the Committee of Council on Education" (two copies):
from the Department.

"Journal of the Photographic Society," for 1865:
from the Society.

"Pharmaceutical Journal and Transactions," for 1865:
from the Editor.

"Proceedings of the British Pharmaceutical Conference," 1864 and 1865: from Dr. Atfield.

"Annual Report of the Leeds Philosophical and Literary Society" (1863-64): from the Society.

"Thirty-second Report of the Royal Cornwall Polytechnic Society" (1864): from the Society.

"Proceedings of the Literary and Philosophical Society of Liverpool" (1863-4): from the Society.

"Journal of the Society of Arts," 1865: from the Society.

"Chemical News" for 1865: from the Editor.

"The Reader" for 1865: from the Editor.

"American Journal of Science and Art," from the November, 1864 to September, 1865: from the Editors.

"Chemical Contributions to the American Journal of Science and Art in the year 1864" by M. Carey Lea: from the Author.

"Journal of the Franklin Institute," from November, 1864 to October, 1865: from the Institute.

"Proceedings of the American Philosophical Society" (1865): from the Society.

"Catalogue of the Library of the American Philosophical Society:" from the Society.

"Transactions of the Albany Institute," vol. IV: from the Institute.

"Transactions of the Society for the Promotion of Useful Arts in the State of New York," vol. IV, part 2: from the Society.

"Proceedings of the Academy of Natural Sciences at Philadelphia" (1864): from the Academy.

"Smithsonian Contributions to Knowledge," vol. XIV.

"Annual Report of the Board of Regents of the Smithsonian Institution" (1865): from the Smithsonian Institution.

"Report of the Commissioner of Patents (United States) for the years 1860, 1861, 1862, and Introductory Report for 1863:" from the Commissioner.

"Journal of the Argentine Pharmaceutical Society" (1863): from the Society.

"Les Mondes," Tome VI, Nos. 16-18: from the Abbé Moigno.

"Cosmos," 2me Série, Tomes I et Tome II, Livraisons 1—24: from the Editor.

"Bulletin de l'Académie des Sciences de St. Pétersbourg,"

Tome V, Feuilles 9–36; Tome VI, Feuilles 1–32; Tome VII, Feuilles 1–36; Tome VIII, Feuilles 1–36:
from the Academy.

"Bulletin de l'Académie royale de Belgique," 1864, 1865:

"Annuaire de l'Académie royale de Belgique:"
from the Academy.

"Memorie dell'Accademia delle Scienze dell'Istituto di Bologna," Serie 2, Tomo III; Fasciculi, 1–4; Tomo IV, Fasciculo 1: from the Academy.

"Rendiconti delle Sessioni dell'Accademia delle Scienze dell' Istituto di Bologna" (1863–64): from the Academy.

"Memorias de la Real Academia de Ciencias de Madrid," Tomo VI: from the Academy.

"Resumen de les Actas de l'Academia de Ciencias de Madrid" (1862–63): from the Academy.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften in Wien (Math-phys. Classe)," Band XXIII.

"Sitzungsberichte derselben," 1863, Abth. II, Heft 3; 1864, Abth. I, Hefte 1–5; Abth. II, Hefte 1–5; and 1865, Heft 1:
from the Imperial Academy of Sciences at Vienna.

"Sitzungsberichte der Koniglich-Baeyrischen Akademie der Wissenschaften in München," 1864, Band II, Hefte 2, 3: 1865, Bd. I, Hefte 1–4; Bd. II, Hefte 1, 2:
from the Royal Bavarian Academy of Sciences.

"Jahrbuch der K. K. geologischen Reichsanstalt zu Wien," Bd. XIV, Hefte 1–4 (Januar—September, 1864); Bd. XV, Hefte 1, 2: from the Institute.

"Zeitchrift für Chemie und Pharmacie," herausgegeben von E. Erlenmeyer, Bd. VII, Hefte 19-23.—Neue Folge, herausgegeben von A. Hübner, Bd. I, Hefte 1–13:
from the Editors.

"Verhandlungen der Naturforschenden Gesellschaft in Basel," Abth. IV, Hefte 1: from the Society.

"Öfversigt af Kongl. Vetenskaps Akademiens Förhandlingar," 1863: from the Royal Academy of Sciences at Stockholm.

"Oversigt over det Kongelige danske Videnskäbernes Selskabs Forhandlinger, og dets Medlemmers Arbeeten" (1864):
from the Royal Danish Academy of Sciences.

INDEX.

A.

Abel, F. A., on the compounds of copper and phosphorus, 249.

Acetate of phenyl: its formation by the action of bisulphide of carbon on a mixture of acetate of lead and phenylic alcohol, 24.

—— of potash, note on the action of chloropicrin and chloroform on: by Henry Bassett, 31.

Acetic anhydride: its formation by the action of bisulphide of carbon on acetate of lead or silver, 22.

Acetic series of acids, the relation of the acrylic series to, 152.

Acid acetic: absorption of its vapour by charcoal, 290.

—— alpha-nitrobenzoic, 313.

—— amidoanisic, 312.

—— amidobenzoic, 34.

—— anisic, formation of, by the action of nitrous acid on diazo-amidoanisic acid, 315.

—— benzoic, action of nitric acid on, 323.

—— —— formation of, by the action of nitrous acid on diazo-amidobenzoic acid, 310.

—— —— simultaneous action of sulphuric and nitric acids on, 325.

—— beta-nitrobenzoic, 323, 326.

—— bromobenzoic, 307.

—— carballylic, 334.

—— chlorobenzoic, 306.

—— chlorotoluylic, 317.

—— diazo-amidoanisic, 311.

—— —— products of decomposition of, 304.

—— —— salts of, 313.

—— diazo-amidobenzoic, 299.

—— —— action of ammonia on, 310.

—— —— action of chlorine, bromine and iodine upon, 306.

—— —— —— haloid acids on, 302.

—— —— —— hydriodic acid on, 305.

—— —— —— nitric acid on, 308.

—— —— —— nitrous acid on, in presence of water, 309.

Acid diazo-amidobenzoic: action of nitrous acid on, in presence of alcohol, 310.

—— —— products of decomposition of, 302.

—— —— salts of, 300.

—— diazo-amidocuminic, 317.

—— diazo-amidotoluylic, 316.

—— ethyl-crotonic, action of potassium-hydrate on, 138.

—— —— formation of, 134.

—— glycollic, formation of from glyoxylic acid, 202.

—— glyoxylic, action of zinc on, 201.

—— —— on some compounds and derivatives of: by H. Debus, 193.

—— —— compound of, with bisulphite of soda, 193.

—— hydriodic: its action on diazo-amidobenzoic acid, 199.

—— —— its action on glyoxylates, 199.

—— hydrochloric, method of demonstrating the composition of, 157.

—— iodanisic, 314.

—— iodobenzoic, 306.

—— iodoxybenzoic, 308.

—— meconic, microscopic characters of, 37.

—— methacrylic, action of potassium-hydrate on, 143.

—— —— formation and properties of, 142.

—— methyl-crotonic, action of potassium-hydrate on, 141.

—— —— formation and properties of, 139.

—— nitric: its action on diazo-amidobenzoic acid, 308.

—— —— benzoic acid, 322.

—— —— nitrobenzoic, 319.

—— nitrous, its action on diazo-amidobenzoic acid, 309.

—— nitric, simultaneous action of, and of sulphuric acid on benzoic acid, 325.

—— —— on β-nitrobenzoic acid, 326.

—— oxalic, formation of, from glyoxylic acid, 202.

—— picramic, formation of diazo-dinitrophenol from, 269.

Acid, sulphuric, simultaneous action of, and of nitric acid on benzoic acid, 325.
—— —— on β-nitrobenzoic acid, 326.
—— thiophosphamic, 5.
—— thiophosphodiamic, 2.
—— tribromobenzoic, 307.
—— tricarballylic, formation of, 332.
—— —— salts of, 337.
—— trinitrobenzoic, 309.
Acids of the acrylic series, names and formation of, 155.
—— —— researches on. No. 1, Transformation of the lactic into the acrylic series of acids: by E. Frankland and B. F. Duppa, 133.
—— haloïd, action of, upon diazo-amidobenzoic acid, 302.
—— on the synthesis of tribasic: by Maxwell Simpson, 331.
Acrylic form of acids, extension of the benzoic series, 154.
—— series, relations of the artificial to the natural acids of the, 147.
—— —— of acids: their relations to the acetic series, 152.
—— —— their relations to the lactic series, 151.
Alcohol-vapour, absorption of, by charcoal, 289.
Alcohols, on caprylic and œnanthylic: by E. T. Chapman, 290.
Aldehyde: its formation from diazo-amidobenzoic acid, 310.
Alkalies, examination of insoluble substances for, 229.
Alkaline salts, solubility of magnesia in, 27.
Allyl-tercyanide, preparation of, 332.
Allylic series of acids, constitution of, 154.
American petroleum, on the most volatile constituents of: by E. Ronalds, 54.
Amidobenzoic hydriodates, α and β, 321.
Ammonia: its action on sulphochloride of phosphorus: by J. H. Gladstone and J. D. Holmes, 1.
—— its action on diazo-amidobenzoic acid, 310.
—— determination of, in waters, 125.
—— method of demonstrating the composition of, 167.
—— gas, absorption of by charcoal, 290.
Ammoniacal compounds of glyoxylates, 196.
—— deposit, on an, formed in the process of drying blood: by J. A. R. Newlands, 340.
Ammonium, diazo-amidoanisate of, 313.
—— diazo-amidobenzoate of, 301.
—— diazo-amidotoluylate of, 316.
Amylic ether, tricarballylic, 335.
Analysis of potable waters, on some points in the: by W. A. Miller, 117.
—— qualitative, notes upon the general routine of, for metals: by C. L. Bloxam, 97.
—— —— of substances insoluble in water and in acids: by C. L. Bloxam, 226.
Anhydrides and ethers, on a new reaction for the production of: by J. Broughton, 21.
Anniversary meeting of the Chemical Society (March 30, 1865), 344.
Arsenate, hydrated plumbo-cupric (bayldonite) from Cornwall, 265.
Arsenious acid, on the action of chlorine on: by C. L. Bloxam, 62.
Atacamite, 80.
—— group, notes on a Cornish mineral of the: by A. H. Church, 214.
Azodinaphthyldiamine, on the action of nascent hydrogen on: by W. H. Perkin, 173.

B.

Balance-sheet of the Chemical Society (1865), 350.
Barium, diazo-amidobenzoate, 301.
—— diazo-amidocuminate, 317.
—— diazo-amidotoluylate of, 316.
—— glyceritricarballylate of, 336.
Bases, on the perioxides of some of the organic: by W. A. Tilden, 99.
Bassett H., note on the action of chloropicrin and chloroform on acetate of potash, 31.
Bayldonite (hydrated plumbo-cupric arsenate) from Cornwall, 265.
Benzoic series, extension of the acrylic form of acids to the, 154.
Benzol-vapour, absorption of, by charcoal, 288.
Bisulphide of carbon: formation of acetic anhydride by its action on acetate of lead or silver, 22.
—— —— formation of acetate of phenyl by its action an a mixture of phenylic alcohol and acetate of lead, 24.
—— —— its action on various salts, 26.
—— —— —— naphthyldiamine, 178.
—— —— vapour, absorption of, by charcoal, 288.
Bisulphite of lime, compound of, with glyoxylate of lime, 194.
—— of soda, compound of, with glyoxylic acid, 193.
Blood, on an ammoniacal deposit formed in the process of drying: by J. A. Newlands, 240.

Bloxam, C. L., on the action of chlorine upon arsenious acid, 62.
—— on the action of hydrosulphate of ammonia upon freshly precipitated sulphide of copper, 94.
—— notes on the general routine of qualitative analysis for metals, 97.
—— on the qualitative analysis of substances insoluble in water and in acids, 226.
Blue colouring matter of indigo, estimation of, 217.
Blunt, T. P., on phosphide of magnesium, 106.
Boiling points of isomeric ethers of the formula $C_nH_{2n}O_2$, note on the: by J. A. Wanklyn, 30.
Botallackite, 215.
Brady H. B., and H. Deane, on microscopical research in relation to pharmacy, 34.
Brine, on a dense, from Saltsprings, Nova Scotia: by Prof. How, 46.
Brochantite, 85.
Bromo-camphor, 92.
Bronzes, analyses of some, found in Great Britain: by A. H. Church, 215.
Broughton, J., on a new reaction for the production of anhydrides and ethers, 21.
Brown, Dr. A. Crum, on the theory of isomeric compounds, 230.
Brown, J. T., Table for the calculation of direct nitrogen determinations, 210.
Butyl-hydride in American petroleum, 60.

C.

Cables (gutta-percha), experiments upon damaged, suspended in air or placed underground, 279.
—— submarine, experiments on, 278.
Cadmium, thiophosphamate of, 6.
—— thiophosphodiamate of, 4.
Caffeine, periodide of, 100.
Calcium-aluminic phosphate, hydrated, from Cornwall, 263.
—— diazo-amidobenzoate of, 301.
Calvert, F. C., on the action of silica and carbonate of soda on cotton fibre, 70.
—— on a crystallised hydrate of phenylic alcohol, 66.
Camphor, on a new bromine-derivative of, by W. H. Perkin, 92.
Caoutchouc, on the decay of: by W. A. Miller, 280.
Capryl, bromide of, 293.
Caprylic and œnanthylic alcohols, on: by E. T. Chapman, 290.
Carbon, formation of acetic anhydride by the action of bisulphide of, on acetates, 22.
—— formation of acetate of phenyl by the action of bisulphide of, on a mixture of acetate of lead and phenylic alcohol, 24.
—— action of bisulphide of, on various salts, 26.
Carbonate and silicate of soda, action of, on cotton fibre: by F. C. Calvert, 70.
Carbonic acid vapour, absorption of, by charcoal, 290.
Castor oil alcohols, 290.
Cerous phosphate, hydrated, from Cornwall, 259.
Chapman, E. T., on caprylic and œnanthylic alcohols, 290.
Charcoal, on the absorption of vapours by: by John Hunter, 285.
Chemical combination: its influence on specific refractive energy, 113.
Chemical Society, balance sheet of the (1865), 350.
—— —— donations to the library of the (1865), 355.
—— —— proceedings at the meetings of the (1865), 342.
Chlorine, on the action of, on arsenious acid: by C. L. Bloxam, 62.
Chloropicrin and chloroform, note on the action of, on acetate of potash: by Henry Bassett, 31.
Chloropropionate ethylic, formation of, from ethylic lactate, 144.
Chloroform-vapour, absorption of, by charcoal, 290.
Church A. H., analyses of some bronzes found in Great Britain, 215.
—— notes on a Cornish mineral of the atacamite group, 212.
—— on a ferric hydrate from Cornwall, 214.
—— on some hydrated cupric oxychlorides from Cornwall, 77.
—— on some hydrated cupric oxysulphates from Cornwall, 83.
—— chemical researches on some new and rare Cornish minerals, 259.
Codeine, microscopical characters of, 36.
Colour of a water, mode of observing the, 118.
Copper, action of hydrosulphate of ammonia on sulphide of, 94.
—— and phosphorus, on the compounds of: by F. A. Abel, 249.
—— diazo-amidobenzoate of, 301.
—— thiophosphamate of, 3.
—— tricarballylate of, 338.
Cornbrash, manganese in, 207.
Cupric ethylcrotonate, 137.

Cupric oxychlorides and oxysulphates from Cornwall, on some hydrated: by A. H. Church, 77, 83.

D.

Deane, H. and H. B. Brady, on microscopical research in relation to pharmacy, 34.
Debus, H., on some compounds and derivatives of glyoxylic acid, 193.
Diazo-amidoanisates, 313.
—— amidobenzoates, 301.
—— amidotoluates, 316.
—— dinitrophenol, 268, 298.
—— nitrochlorophenol, 271.
—— nitrophenol, 270.
Diethoxalate, ethylic, action of trichloride of phosphorus, on, 135.
Dimethoxalate, ethylic, action of trichloride of phosphorus, on, 141.
Dinitrotoluol, formation of, 320.
Donations to the Library of the Chemical Society (1865), 355.
Duppa B. F., and E. Frankland, researches on acids of the acrylic series.—No. 1. Transformation of the lactic into the acrylic series of acids, 133.

E.

Ethers and anhydrides, on a new reaction for the production of: by J. Broughton, 21.
—— isomeric, of the formula $C_nH_{2n}O_2$; note on their boiling points: by J. A. Wanklyn, 30.
—— tricarballylic, 335.
Ether vapour: its absorption by charcoal, 289.
Ethomethoxalate, ethylic action of trichloride of phosphorus on ethylic, 139.
Ethyl-caffeine, periodide of, 102.
—— crotonate, cupric, 137.
—— —— ethylic, 134.
—— —— of lead, 137.
—— —— of silver, 136.
—— diazo-amidoanisate, 314.
—— diazo-benzoate, 301.
—— hydride in American petroleum, 56.
Ethylic chloropropionate, formation of, 144.
—— diethoxalate, action of trichloride of phosphorus, on, 133.
—— dimethoxalate, 141.
—— ethomethoxalate, 139.
—— ethyl-crotonate, formation and properties of, 134.
—— lactate, action of trichloride of phosphorus, on, 145.
Ethylic leucate, 133.
—— methacrylate, formation and properties of, 143.
—— methylcrotonate, 139.
Evaporation of waters and incineration of the residue, 119.

F.

Ferric hydrate, notes on a, from Cornwall: by A. H. Church, 214.
Ferricyanide of potassium: its action on ferric salts, 27.
Forest marble of Cirencester, manganese in, 207.
Fousel-oil vapour, absorption of, by charcoal, 289.
Frankland, F. and B. F. Duppa, researches on acids of the acrylic series.—No. 1. Transformation of the lactic into the acrylic series of acids, 133.

G.

Gaseous constituents of waters, estimation of, 124.
Gladstone, J. H., on the specific refractive energy of elements and their compounds, 108.
Gladstone, J. H., and J. D. Holmes, on the action of ammonia on sulphochloride of phosphorus, 1
Glycerl-tricarballylate of baryta, 336.
Glyoxylate of lead and ammonia, 198.
—— lime and ammonia, 196.
—— —— with bisulphite of lime, 194.
—— —— lactate of lime, 195.
—— silver and ammonia, 198.
Glyoxylates, action of hydriodic acid on, 198.
—— —— sulphuretted hydrogen on, 199.
—— ammoniacal compounds of, 197.
Griess, P., on a new series of bodies in which nitrogen is substituted for hydrogen, 268, 298.
Gutta-percha, on the decay of: by W. A. Miller, 273.
Gutta, pure, experiments on, 274.

H.

Hardness of waters, determination of, 119.
Hexphosphide of copper, 250.
Hofmann, A. W., on lecture illustrations, 156.

Holmes, J. D., and J. H. Gladstone, on the action of ammonia on sulphochloride of phosphorus, 1.
How, Prof., on a dense brine from Salt-springs, Nova Scotia, 46.
Hunter, John, on the absorption of vapours by charcoal, 285.
Hydrated calcium-aluminic phosphate from Cornwall, 263.
—— cerous phosphate from Cornwall, 259.
—— plumbo-cupric arsenate (bayldonite) from Cornwall, 265.
Hydride of butyl in American petroleum, 60.
Hydrides of ethyl and propyl in American petroleum, 56.
Hydrochloric acid, mode of demonstrating the composition of, 157.
Hydrogen, on the action of nascent, on azodinaphthyldiamine: by W. H. Perkin, 173.
Hydrosulphate of ammonia: its action on freshly precipitated sulphide of copper, 94.

I.

Incineration of the fixed residue of waters, 119.
India-rubber, on the oxidation of: by J. Spiller, 44. (See also p. 280.)
Indigotin, or blue colouring matter of indigo, on the estimation of: by Cl. Ullgren, 217.
Insoluble substances, examination of, for alkalies, 229.
Iodostrychnine, periodide of, 105.
Isomeric compounds, on the theory of: by Dr. A. Crum Brown, 230.
—— ethers of the formula of $C_nH_{2n}O_2$, note on the boiling points of: by J. A. Wanklyn, 30.
Isomerism, remarks on: by E. J. Mills, 329.

K.

Kelloway rock, manganese in, 207.

L.

Lactate, ethylic, action of terchloride of phosphorus on, 144.
—— of lime, compound of, with glyoxylate of lime, 195.
Lactic series of acids, relations of the acrylic to, 151.
—— —— transformation of, into the acrylic series, 133.
Langite, 87.
Lead, on the action of light on sulphide of, and its bearing on the preservation of paintings in picture galleries: by D. S. Price, 245.
—— estimation of, in waters, 129.
—— ethylcrotonate, 137.
—— glyoxylate of, and ammonia, 198.
—— thiophosphamate of, 6.
—— tricarballylate of, 338.
Lecture illustrations, on: by A. W. Hofmann, 156.
Leucate, action of terchloride of phosphorus on ethylic, 133.
Lias and oolite, on the presence of manganese in: by R. Warington, jun., 206.
Library of the Chemical Society, donations to the (1865), .
Light, on the action of, on sulphide of lead, 245.
Lime, glyoxylate of, and ammonia, 196.
—— glyoxylate of, with bisulphite of lime, 194.
—— —— lactate of lime, 195.
Liquor Opii sedativus, microscopical characters of, 39.
Lyellite, 83.

M.

McDougall, A., on a mode of measuring the relative sensitiveness of photographic papers, 183.
Magnesia, solubility of, in alkaline salts, 27.
Magnesium, diazo-amidoanisate of, 314.
—— diazo-amidobenzoate of, 301.
—— on phosphide of: by T. P. Blunt, 106.
Manganese, on the presence of, in oolite and lias, 206.
Marsh gas, method of demonstrating the composition of, 171.
Meconate of morphine, microscopical appearance of, 36.
Meconin, microscopical appearance of, 37.
Meetings of the Chemical Society, proceedings at the (1865), 342.
Metals, notes upon the general routine of qualitative analysis for: by C. L. Bloxam, 97.
Methacrylates, 142.
Methyl-alcohol vapour, absorption of by charcoal, 288.
Methyl-caffeine, iodide and periodide of, 103.
Methyl-crotonates, 140.
Methyl, diazo-amidoanisate of, 314.
—— diazo-amidobenzoate of, 302.
Microscopical research in relation to

pharmacy: by H. Deane and H. B. Brady, 34.
Miller, W. A., observations on some points in the analysis of potable waters, 117.
—— on the decay of gutta-percha and caoutchouc, 173.
Mills, E. J. on nitro-compounds (Part II), with remarks on isomerism, 319.
Minerals, on some new and rare Cornish: by A. H. Church, 259.
Mixture and solution: their influence on the specific refractive energy of elements and their compounds, 108.
Morphine: microscopical appearance of its meconate and sulphate, 36.

N.

Naphthalene, on the formation of pyridine from: by W. H. Perkin, 9.
Naphthene-diamine, 181.
Naphthylamine, formation of, from azodinaphthyldiamine, 181.
Naphthyldiamine, 175.
—— its behaviour with oxidising agents, 178.
—— hydrochlorate of, 176.
—— nitrate of, 178.
—— oxalate of, 178.
—— sulphate of, 177.
Narceine, microscopical characters of, 36.
Narcotine, microscopical characters of, 37.
Neilson, J. B., obituary notice of, 345.
Newlands, J. A. R., on an ammoniacal deposit formed in the process of drying blood, 340.
Nitrites, estimation of, in waters, 127.
Nitro-compounds, on: by E. J. Mills, 319.
Nitrogen: on a new series of bodies in which it is substituted for hydrogen: by P. Griess, 268, 298.
Nitrogen determinations, table for the calculation of, 210.
Normandy, Dr., obituary notice of, 345.

O.

Obituary notice of J. B. Neilson, 345.
—— Dr. Normandy, 345.
—— Dr. E. Pugh, 346.
—— Dr. R. D. Thomson, 344.
Odour of waters, mode of observing, 118.
Œnanthylic and caprylic alcohols, on: by E. T. Chapman, 290.
Oolite and lias, on the presence of manganese in: by R. Warington, junr., 206.
Opium, microscopical characters of its various preparations, 38.
Organic bases, on the periodides of some of the: by W. A. Tilden, 99.
Organic matter, determination of, in waters by incineration, 119.
—— —— by potassic permanganate, 120.
Oxidation of india-rubber: by J. Spiller, 44. (See also p. 280.)
Oxychlorides and oxysulphates, on some hydrated, from Cornwall: by A. H. Church, 77, 83.

P.

Paintings, on the action of light on sulphide of lead, and its bearing on the preservation of, in picture galleries: by D. S. Price, 245.
Papaverine, microscopical characters of, 37.
Periodides of some of the organic bases, on the: by W. A. Tilden, 99.
Perkin, W. H., on a new bromine deviative of camphor, 92.
—— on the action of nascent hydrogen on azodinapthyldiamine, 173.
—— note on the formation of pyridine from naphthalene, 9.
Permanganate potassic, use of, for estimating organic matters in waters, 120.
Petroleum, Canadian, caprylic alcohol from, 296.
—— on the most volatile constituents of American: by E. Ronalds, 54.
Pharmacy, on microscopical research in relation to: by H. Deane and H. B. Brady, 34.
Phenylic alcohol, on a crystallised hydrate of: by F. C. Calvert, 66.
Phosphate, calcium-aluminic, from Cornwall, 263.
—— hydrated cerous, from Cornwall, 259.
Phosphide of magnesium, on: by T. P. Blunt, 106.
Phosphorus, the action of ammonia on sulphochloride of: by J. H. Gladstone and J. D. Holmes, 1.
—— on the compounds of copper and: by F. A. Abel, 249.
—— terchloride of: its action on ethylic diethoxalate, 133.
—— —— dimethoxalate, 141.
—— —— ethomethoxalate, 139.
—— —— lactate, 145.
—— —— leucate, 133.
Photographic papers, on a mode of measuring the relative sensitiveness of: by A. McDougall, 183.

Platinopyridine, bihydrochlorate of, 180.
Plumbo-cupric arsenate (bayldonite) from Cornwall, 265.
Potable waters, on some points in the analysis of: by W. A. Miller, 117.
Potash, note on the action of chloropicrin and chloroform on the acetate of: by H. Bassett, 21.
Potassium, diazo-amidoanisate of, 313.
—— diazo-amidobenzoate of, 301.
—— diazo-amidotoluylate of, 316.
Potassium-hydrate: its action on ethyl-crotonic acid, 138.
—— —— methacrylic acid, 143.
—— —— methyl-crotonic acid, 141.
Price, D. S., on the action of light on sulphide of lead, and its bearing on the preservation of paintings in picture galleries, 245.
Proceedings at the meetings of the Chemical Society (1865), 342.
Propyl-hydride in American petroleum, 56.
Pugh, Dr. E., obituary notice of, 346.
Pyridine, on the formation of, from naphthalene: by W. H. Perkin, 9.
—— formation of from azodinapthyldiamine, 180.

Q.

Qualitative analysis, notes on the general routine of, for metals: by C. L. Bloxam, 97.
—— of substances insoluble in water and in acids: by C. L. Bloxam, 226.

R.

Refractive energy of elements and their compounds, on the specific: by J. H. Gladstone, 108.
Report of the President and Council,
—— Treasurer,
Ronalds, E., on the most volatile constituents of American petroleum, 54.

S.

Saline constituents of waters, estimation of, 129.
Saltsprings, Nova Scotia, on a dense brine from: by Prof. How, 46.
Sediment, determination of amount of, in waters, 118.
Silicate and carbonate of soda, action of, on cotton fibre: by F. C. Calvert, 70.
Silver, diazo-amidobenzoate of, 301.
—— diazo-amidotoluylate of, 316.
—— glyoxylate of, and ammonia, 198.
Silver, tricarballylate of, 338.
—— ethyl-crotonate, 136.
Simpson, Maxwell, on the synthesis of tribasic acids, 331.
Soda-bisulphite, compound of, with glyoxylic acid, 193.
Soda-salts of tricarballylic acid, 337.
Sodium, diazo-amidoanisate of, 313.
—— diazo-amidobenzoate of, 301.
—— diazo-amidotoluylate of, 316.
—— solution and mixture: their influence on the specific refractive energy of elements and their compounds, 110.
Specific refractive energy of elements and their compounds: by J. H. Gladstone, 108.
Spiller, J., on the oxidation of india-rubber, 34.
Sprengel, H., researches on the vacuum, 9.
Sulphide of copper, action of hydrosulphate of ammonia on, 94.
Sulphide of lead, on the action of light on, and its bearing on the preservation of paintings in picture galleries: by D. S. Price, 245.
Sulphochloride of phosphorus, the action of ammonia on: by J. H. Gladstone and J. D. Holmes, 1.
Sulphuretted hydrogen: its action on glyoxylates, 199.
Synthesis of tribasic acids, on the: by Maxwell Simpson, 331.

T.

Taste of waters, observation of, 118.
Temperature: its influence on the specific refractive energy of elements and their compounds, 109.
Terchloride of phosphorus: its action on ethylic diethoxalate, 133.
—— —— dimethoxalate, 141.
—— —— ethomethoxalate, 139.
—— —— lactate, 145.
—— —— leucate, 133.
Tercyanide of allyl, preparation of, 332.
Thebaine, microscopical characters of, 37.
Thiophosphamate of cadium, 6.
—— lead, 6.
Thiophosphodiamate of cadmium, 4.
—— copper, 3.
—— zinc, 4.
Thomson, R. D., obituary notice of, 344.
Tilden, W. A., on the periodides of some of the organic bases, 99.
Tribasic acids, on the synthesis of: by Maxwell Simpson, 331.

Tricaprylamine, 294.
Tricarballylic ethers, 335.

U.

Ullgren, Cl., on the estimation of indigotin, or the blue colouring matter of indigo, 217.

V.

Vacuum, researches on the: by H. Sprengel, 9.
Vapour-densities, on: by J. A. Wanklyn, 89.
Vapours, on the absorption of, by charcoal: by John Hunter, 285.

W.

Wanklyn, J. A., note on the boiling points of isomeric ethers of the formula $C_nH_{2n}O_2$, 30.
Wanklyn, J. A., on vapour densities, 89.
Warington, R., jun., laboratory memoranda:
I. The action of ferricyanide of potassium on ferric salts, 27.
II. The solubility of magnesia in alkaline salts, 27.
—— on the presence of manganese in oolite and lias, 206.
Water, method of demonstrating the composition of, 164.
Waters, on some points in the analysis of potable: by W. A. Miller, 117.
Water-vapour, absorption of, by charcoal, 290.

Z.

Zinc, its action on glyoxylic acid, 201.
—— thiophosphodiamate of, 4.

ERRATA.

Page.	Line.	
127	1	*dele* "ten."
127	9	from bottom *for* 0·00237 *read* 0·000237.
293		The last line should be transferred to the top of page 295.